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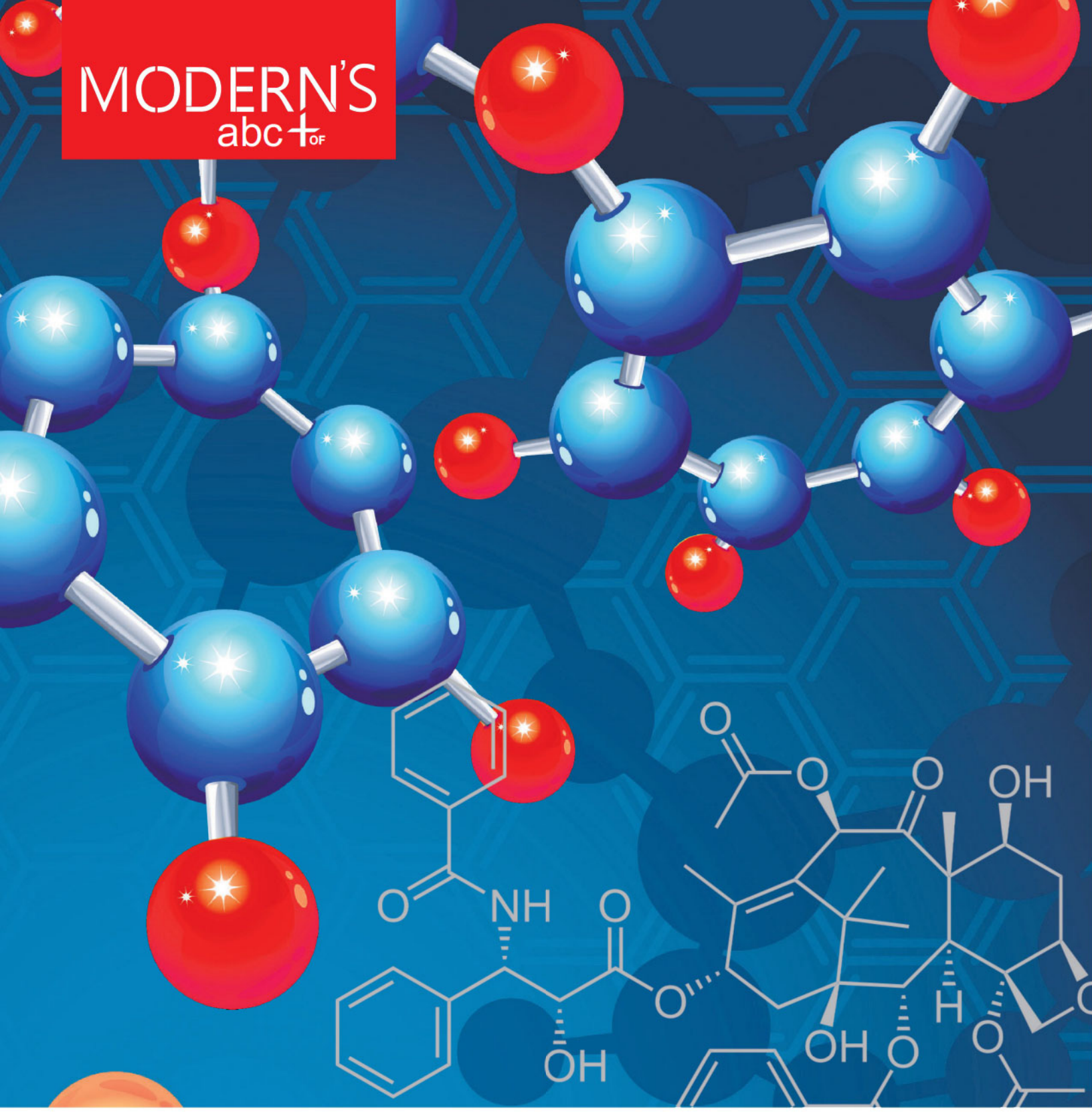

CHEMISTRY

CLASS-XI

PART I & II

STRICTLY ACCORDING TO THE NEW SYLLABUS

INDIA'S FIRST SMART BOOK

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Dr. S.P. Jauhar

According to new syllabus prescribed by Central Board of Secondary Education (CBSE), New Delhi and State Boards of Uttarakhand, Karnataka (Ist Year PUC), Chhattisgarh, Jharkhand, Punjab, Haryana, Himachal, Kerala, Mizoram, Meghalaya, Nagaland, Assam, Manipur and other States following CBSE & ISC curriculum.

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CHEMISTRY

INDIA'S FIRST SMART BOOK

Strictly in accordance with the Latest Guidelines and Syllabus issued by N.C.E.R.T. / C.B.S.E.

For Class XI

PART-II

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REDOX REACTIONS

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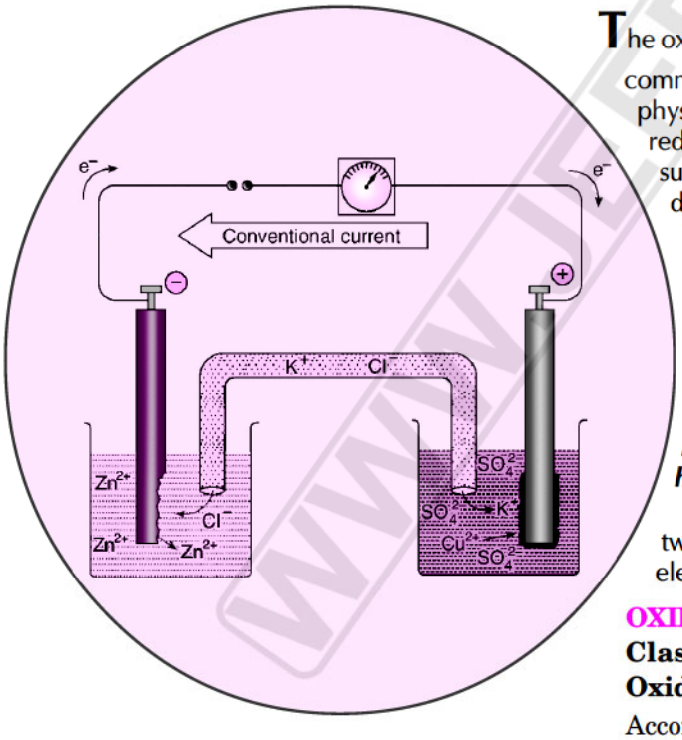

The oxidation and reduction reactions or **redox reactions** are very common in our daily life. A large number of phenomena both physical as well as chemical and biological are concerned with redox reactions. Chemical reactions like burning of coal, sulphur, cooking gas, rusting of iron, generation of electricity, digestion of food, etc are examples of redox reactions. Many industrial processes such as electroplating, production of *caustic soda, potassium permanganate, extraction of metals like sodium, iron and aluminium*, etc are also common examples of redox reactions. In fact, **redox reactions keep us alive.** They help to capture the energy of the sun by the photosynthesis process by plants which is used by us. Recently, environmental issues such as ***hydrogen economy*** *i.e.,* use *of liquid hydrogen as fuel and development of* ***ozone hole*** are considered as redox phenomena.

In the present unit, we shall classify the reactions into two classes, oxidation and reduction reactions and discuss electrochemical cells.

OXIDATION AND REDUCTION REACTIONS

Classical Concepts of Oxidation and Reduction

Oxidation

According to classical (earlier) views, **oxidation** is defined as ***the addition of oxygen or any other electronegative element or removal of hydrogen or any other electropositive element.***

For example, the oxidation reactions are :

(*i*) $C + O_2 \longrightarrow CO_2$

(*ii*) $2Mg + O_2 \longrightarrow 2MgO$

} Addition of oxygen

(*iii*) $Zn + S \longrightarrow ZnS$

(*iv*) $Mg + Cl_2 \longrightarrow MgCl_2$

} Addition of electronegative element

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The above reactions involve addition of oxygen or electronegative element (S and Cl_2) and therefore, are oxidation reactions.

(v) $2H_2S + O_2 \longrightarrow 2H_2O + 2S$ } Removal of hydrogen

(vi) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

(vii) $2KI + Cl_2 \longrightarrow 2KCl + I_2$ } Removal of electropositive element

$(viii)$ $2K_4[Fe(CN)_6] + H_2O_2 \longrightarrow 2K_3[Fe(CN)_6] + 2KOH$

These reactions involve removal of hydrogen or some electropositive element (potassium) and, therefore, are oxidation reactions.

In these reactions, the substances shown coloured have undergone oxidation.

Oxidising Agent or Oxidant

A substance which gives oxygen or removes hydrogen is called an **oxidising agent** or **oxidant.**

For example, in examples (i) and (ii), O_2 is an oxidising agent because it causes the oxidation of C and Mg. Similarly, in reactions (iii) and (iv) S and Cl_2 act as oxidising agents because they add electronegative element to Zn and Mg. Similarly, Cl_2 and MnO_2 act as oxidising agents in reactions (v) and (vi) because they remove hydrogen while, Cl_2 and H_2O_2 act as oxidising agents in reactions (vii) and $(viii)$ because they remove electropositive element (potassium).

Reduction

According to classical concept, **reduction** is defined as

the addition of hydrogen or any other electropositive element or removal of oxygen or any other electronegative element.

For example, the reduction reactions are :

(i) $Cl_2 + H_2 \longrightarrow 2HCl$ } Addition of hydrogen

(ii) $Br_2 + H_2S \longrightarrow 2HBr + S$

(iii) $2FeCl_3 + Fe \longrightarrow 3FeCl_2$ } Addition of electro-positive element

(iv) $2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$

In the above examples, reactions (i) and (ii) involve addition of hydrogen and reactions (iii) and (iv) involve addition of electropositive elements (Fe and Hg) and therefore, are reduction reactions. Similarly,

(v) $CuO + H_2 \longrightarrow Cu + H_2O$ } Removal of oxygen

(vi) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

(vii) $2FeCl_3 + H_2 \longrightarrow 2FeCl_2 + 2HCl$ } Removal of electronegative element

$(viii)$ $SiCl_4 + 4Na \longrightarrow Si + 4NaCl$

In these examples, reactions involve removal of oxygen or electronegative element (chlorine) and therefore, are reduction reactions.

The substances shown coloured have undergone reduction.

Reducing Agent

A substance which provides hydrogen or removes oxygen *is called* ***a reducing agent*** *or* ***reductant.***

For example, in examples (i) and (ii), H_2 and H_2S act as reducing agents because these cause reduction of Cl_2 and Br_2. Similarly, in reactions (iii) and (iv), Fe and $SnCl_2$ act as reducting agents because these add electropositive elements Fe and Hg. Similarly, in reactions (v) and (vi), H_2 and CO act as reducing agents because these remove oxygen from CuO and Fe_2O_3, respectively. In reactions (vii) and $(viii)$, H_2 and Na act as reducing agents because these remove electronegative element (Cl) from $FeCl_3$ and $SiCl_4$.

Oxidation-Reduction Reactions are Complementary : go side by side

Oxidation-reduction reactions are complementary reactions. Whenever any substance is oxidised, another substance is always reduced at the same time and vice versa. In other words, the oxidation reduction reactions always occur simultaneously i.e., they always go hand in hand or side by side. For example, consider the reaction :

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

In this reaction, stannous chloride ($SnCl_2$) has been oxidised to stannic chloride ($SnCl_4$) because of addition of electronegative element chlorine to it. At the same time $HgCl_2$ is reduced to Hg_2Cl_2 because of the addition of mercury to mercuric chloride. Thus, $SnCl_2$ is oxidised by $HgCl_2$ and $HgCl_2$ is reduced by $SnCl_2$. Hence, $HgCl_2$ acts as an oxidising agent and $SnCl_2$ acts as a reducing agent in this reaction.

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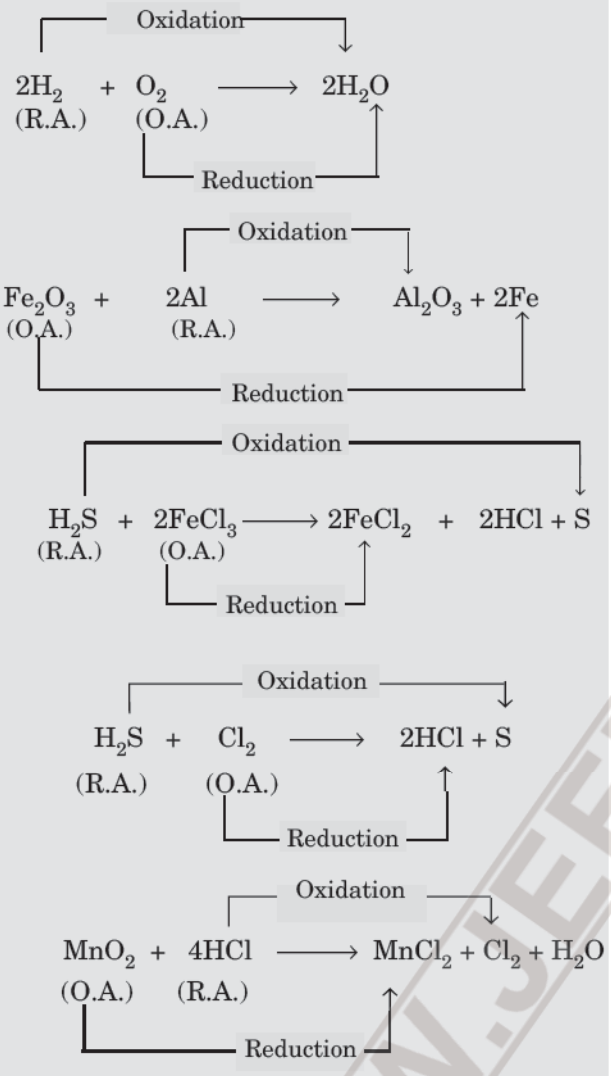
Thus, oxidation and reduction reactions are collectively called **redox reactions**. Some more examples of redox reactions are given below :



Here O.A. and R.A. stand for oxidising agent and reducing agent respectively.

Electronic Concept of Oxidation and Reduction

Oxidation and reduction reactions are now used in a much broader and general sense. These are defined in terms of electron transfer between the reactants, known as electronic concept of oxidation and reduction.

Oxidation. According to electronic concept, **oxidation** *is*

a process which involves loss of electrons by an atom or group of atoms.

As a result of loss of electrons, there is increase in positive charge or decrease in negative charge of the atom or ion undergoing oxidation.

For example,

(*i*) *Loss of electrons resulting in increase in positive charge.*

$$Na \longrightarrow Na^+ + e^-$$
$$Mg \longrightarrow Mg^{2+} + 2e^-$$
$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

(*ii*) *Loss of electrons resulting in decrease of negative charge.*

$$MnO_4^{2-} \longrightarrow MnO_4^- + e^-$$
$$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e^-$$
$$2Cl^- \longrightarrow Cl_2 + 2e^-$$
$$S^{2-} \longrightarrow S + 2e^-$$

Reduction . According to electronic concept, **reduction** *is*

a process which involves gain of electrons by an atom or group of atoms.

Due to gain of electrons there is increase of negative charge or decrease of positive charge of an atom or ion undergoing reduction. For example,

(*i*) *Gain of electrons resulting in decrease of positive charge.*

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$
$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$$
$$Sb^{5+} + 2e^- \longrightarrow Sb^{3+}$$

(*ii*) *Gain of electrons resulting in increase of negative charge.*

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$
$$S + 2e^- \longrightarrow S^{2-}$$
$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$
$$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$$

OXIDATION-REDUCTION REACTIONS AS ELECTRONS TRANSFER REACTIONS

As already learnt, oxidation process involves loss of electrons whereas reduction process involves gain of electrons. During transfer of electrons in a reaction, the species which loses electrons is said to be *oxidised* and the species which gains electrons is said to be *reduced.* Since there cannot be a net loss or gain of electrons in a chemical reaction, this means that all chemical changes involving the loss and gain of electrons occur simultaneously *i.e.* one species loses electrons in oxidation while the other gains electrons during the reduction. Thus, both these changes take place side by side *i.e.,* **oxidation takes place at the cost of reduction and *vice versa.***

In other words, oxidation and reduction reactions go hand in hand. This may be illustrated by the following reactions:

$$4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$$
$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$
$$2Na(s) + S(s) \longrightarrow Na_2S(s)$$

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All these reactions are redox reactions because in each of these reactions sodium is oxidised due to addition of either oxygen or more electronegative elements such as chlorine or sulphur to sodium. Simultaneously oxygen, chlorine and sulphur are reduced because electropositive element sodium has been added to each of these. We have also learnt in chemical bonding that sodium oxide, sodium chloride and sodium sulphide are ionic compounds and may be written as :

Sodium oxide : $(Na^+)_2O^{2-}$, Sodium chloride : $Na^+ Cl^-$, Sodium sulphide : $(Na^+)_2 S^{2-}$.

These ionic charges suggest that the above redox reactions may also be written as :

Loss of $4e^-$: oxidation

$$4Na(s) + O_2(g) \longrightarrow 2(Na^+)_2 O^{2-}(s)$$

Gain of $4e^-$: reduction

Loss of $2e^-$: oxidation

$$2Na(s) + Cl_2(g) \longrightarrow 2Na^+ Cl^-(s)$$

Gain of $2e^-$: reduction

Loss of $2e^-$: oxidation

$$2Na(s) + S(s) \longrightarrow (Na^+)_2 S^{2-}(s)$$

Gain of $2e^-$: reduction

For the sake of convenience, each of the above redox reaction may be considered as the sum of two half reactions; one *involving loss of electrons i.e.* oxidation and the other *involving gain of electrons i.e.* reduction as

$$Na(s) \longrightarrow Na^+ + e^-$$

Oxidation half reaction

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

Reduction half reaction

These two half reactions are called **oxidation half reaction** and **reduction half reaction** respectively. The sum of the half reactions give the overall reaction. It may be noted that the overall reaction is so written that the electrons are balanced *i.e., the number of electrons lost and gained become equal*. This means that the two half reactions are simply added if the number of electrons lost during oxidation half reaction is equal to the number of electrons gained during reduction half reaction. But if the number of electrons lost during oxidation half reaction are different from the number of electrons gained during reduction half reaction, the two half reactions are multiplied by suitable integers so that when the two half equations are added, the electrons get cancelled out in the final redox reaction. For example,

$$Na(s) \longrightarrow Na^+ + e^-] \times 4$$

Oxidation half reaction

$$O_2(g) + 4e^- \longrightarrow 2O^{2-}$$

Reduction half reaction

$$4Na(s) + O_2(g) \longrightarrow 2(Na^+)_2O^{2-} \text{ or } 2Na_2O$$

Overall redox reaction

Similarly, we may write other reactions as :

$$Na(s) \longrightarrow Na^+ + e^-] \times 2$$

Oxidation half reaction

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-$$

Reduction half reaction

$$2Na(s) + Cl_2(g) \longrightarrow 2Na^+Cl^-(s) \text{ or } 2NaCl$$

Overall redox reaction

$$Na(s) \longrightarrow Na^+ + e^-] \times 2$$

Oxidation half reaction

$$S(s) + 2e^- \longrightarrow S^{2-}$$

Reduction half reaction

$$2Na(s) + S(s) \longrightarrow (Na^+)_2 S^{2-}(s) \text{ or } Na_2S(s)$$

Overall redox reaction

In all the above reactions, electrons are transferred from sodium to O_2, Cl_2 and S. Thus, **oxidation-reduction *i.e.*, redox reactions are regarded as electron transfer reactions.** Moreover, we observe that O_2, Cl_2 and S have gained electrons only if there is another substance which can donate electrons. This means that **reduction can occur only if oxidation is occurring side by side and vice versa.** In these reactions, sodium loses electrons and has been oxidised to sodium ion, Na^+. This is brought about by the acceptance of electrons by oxygen, chlorine or sulphur, which get reduced. Thus, oxygen, chlorine and sulphur bring about the oxidation and are called **oxidising agents** or **oxidants.**

Thus, according to electronic concept,

oxidising agent *is a substance which can accept one or more electrons.*

Similarly, in the above example, oxygen, chlorine and sulphur are reduced to oxide ion (O^{2-}), chloride ion (Cl^-) and sulphide ion (S^{2-}) respectively. This has been possible by furnishing electrons by sodium. Thus, sodium is a **reducing agent** or **reductant**. Thus,

reducing agent *is a substance which can give one or more electrons.*

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TO SUM UP

Oxidation is a process in which one or more electrons are lost.

Reduction is a process in which one or more electrons are gained.

Oxidising agent or **oxidant** is a substance which can accept one or more electrons.

Reducing agent or **reductant** is a substance which can give one or more electrons.

In a redox reaction, **oxidising agent** is **reduced** by accepting electrons and **reducing agent** is **oxidised** by losing electrons.

TYPES OF REDOX REACTIONS

The redox reactions may be classified into two types:

1. Direct redox reactions. The reactions in which the oxidation and reduction take place in the same vessel are called **direct redox reactions.**

2. Indirect redox reactions. The reactions in which oxidation and reduction take place in different vessels are called **indirect redox reactions.** These are very important reactions because these form the basis of electrochemical cells.

DIRECT REDOX REACTIONS: REDOX REACTIONS IN AQUEOUS SOLUTIONS

Redox reactions are very common in our daily life. Whenever you use a battery, a redox reaction occurs. A simple example of an oxidation-reduction reaction is the reaction between zinc metal and copper (II) salt in aqueous solution :

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

Let us study this reaction.

Take a strip of zinc metal and clean it with a sand paper. Place this strip in a solution of copper sulphate in a beaker [Fig. 1]. We observe that a spontaneous reaction takes place and the following observations are made :

(*i*) Zinc metal starts dissolving and it loses its weight gradually.

(*ii*) The copper metal starts getting either deposited on the zinc plate or settles down at the bottom of the beaker.

(*iii*) The blue colour of the solution gradually fades away.

(*iv*) The reaction is exothermic and proceeds with the liberation of heat energy.

(*v*) The solution remains electrically neutral.

Let us try to explain the above reaction. In aqueous solution, $CuSO_4$ dissociates into Cu^{2+} and SO_4^{2-} ions. When a strip of zinc is dipped in $CuSO_4$ solution, zinc metal loses electrons and gets oxidised whereas Cu^{2+} ions accept electrons and get reduced. Since zinc is getting oxidised and converted to Zn^{2+} ions which go into the solution, the weight of zinc plate gradually decreases. On the other hand, Cu^{2+} ions present in the solution are accepting the electrons given by zinc and are getting reduced to copper. As a result, copper metal either gets deposited on the zinc plate or gets precipitated at the bottom of the beaker [Fig. 1(*b*)]. Since Cu^{2+} ions from the solution are changing to Cu(*s*), the blue colour of the solution (which is due to Cu^{2+} ions) slowly fades.

The reaction may be written as :

$$Zn(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq) + SO_4^{2-}$$

Formation of Zn^{2+} ions among the products can easily be tested when the blue colour of the solution due to Cu^{2+} ions has disappeared. If we pass, hydrogen sulphide (H_2S) gas through the solution, formation of white precipitate of zinc sulphide (ZnS) on making the solution alkaline with ammonia indicates the presence of Zn^{2+} ions in the solution.

In this reaction, sulphate ions, SO_4^{2-} do not participate and we may write the reaction as :

Loss of $2e^-$: Oxidation

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Gain of $2e^-$: Reduction

or $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

The reaction is commonly described as zinc having displaced Cu^{2+} ions from the $CuSO_4$ solution.

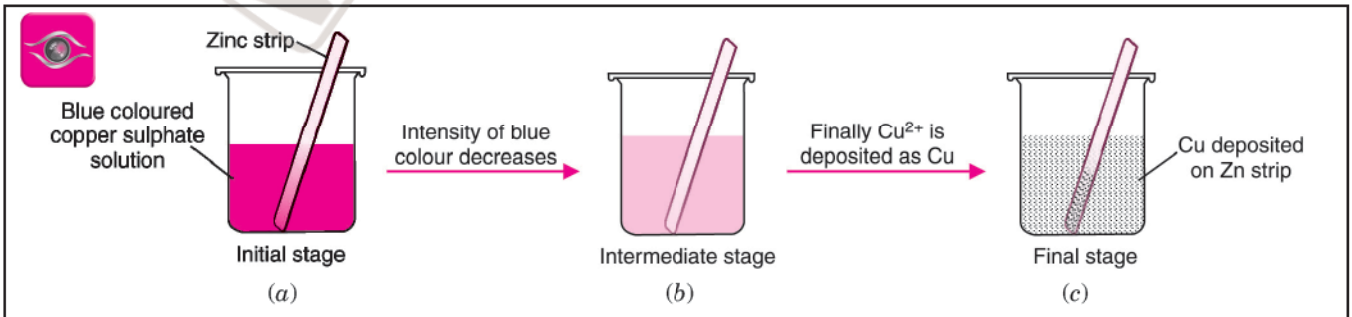

Fig. 1. Redox reaction occurring in a beaker.

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In this case, **zinc acts as a reducing agent** while **Cu^{2+} ions act as oxidising agent.**

In this redox reaction, the transference of electrons from Zn metal to Cu^{2+} ions is occurring directly because the two are in direct contact. The energy released appears as heat and therefore, it is an exothermic reaction.

Let us study the state of equilibrium for the above reaction. For this purpose, place a rod of copper in zinc sulphate ($ZnSO_4$) solution. You will notice that no visible reaction occurs. If we pass H_2S gas through the solution, there will be no black precipitate of copper sulphide indicating that no reaction has occurred. In other words, the following reaction :

$$Cu(s) + ZnSO_4(aq) \longrightarrow CuSO_4(aq) + Zn(s)$$

does not occur. Thus, we conclude that the state of equilibrium for the above reaction between zinc and copper sulphate greatly favours the products over the reactants.

Similarly, when we dip a copper strip in a silver nitrate solution, copper gets oxidised and goes into the solution whereas Ag^+ ions accept electrons and get reduced (Fig. 2). The reaction may be written as :

$$Cu(s) + 2Ag^+(aq) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$$

Loss of $2e^-$: Oxidation

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

Gain of $2e^-$: Reduction

Thus, copper is oxidised to Cu^{2+} and Ag^+ is reduced to $Ag(s)$. Therefore, copper acts as an oxidising agent or oxidant while silver acts as a reducing agent or reductant.

The equilibrium greatly favours the products $Cu^{2+}(aq)$ and $Ag(s)$.

For the purpose of comparison, let us study the reaction between cobalt metal and nickel sulphate solution. For this, place a rod of cobalt metal in nickel sulphate solution. The following reaction occurs :

Loses $2e^-$: Oxidation

$$Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s)$$

Gains $2e^-$: Reduction

At equilibrium, chemical tests show that both $Ni^{2+}(aq)$ and $Co^{2+}(aq)$ are present in moderate concentration. This means that in this case, neither the reactants [$Co(s)$ and $Ni^{2+}(aq)$] nor the products [$Co^{2+}(aq)$ and $Ni(s)$] are greatly favoured.

Thus, we observe that there is a competition of loss or gain of electrons by metals. This is similar to the competition between various acids to lose a proton (H^+) in water. This similarity suggests that we can develop a table in which the metals and their ions are listed on the basis of their tendency to lose or gain electrons similar to the table in which various acids are arranged according to their acid strengths. For example, we have learnt in above experiments that zinc loses electrons to copper and copper releases electrons to silver. Therefore, the electron releasing tendency of these three metals is in the order :

$$Zn > Cu > Ag$$

Similarly, by comparing the relative tendencies of other metals, we can build a table to arrange the metals in their decreasing or increasing order of losing electrons. This series is called **activity series** or **electrochemical series** and is discussed later.

Some other examples of common redox reactions

When a metal reacts with acids, hydrogen is liberated. For example metals like Zn, Mg, Ni etc. can easily displace hydrogen from dil. HCl.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

This reaction occurs as redox reaction in which metal is oxidised and hydrogen is reduced as :

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{Oxidation}$$

$$2H^+ + 2Cl^- + 2e^- \longrightarrow 2Cl^- + H_2 \quad \text{Reduction}$$

$$Zn + 2H^+ + 2Cl^- \longrightarrow Zn^{2+} + 2Cl^- + H_2$$

In electrolytic process also, redox reaction takes place. For example, during electrolysis of aqueous solution of copper chloride, oxidation and reduction occur as :

$$CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^-$$

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu(s)$ Reduction

At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$ Oxidation

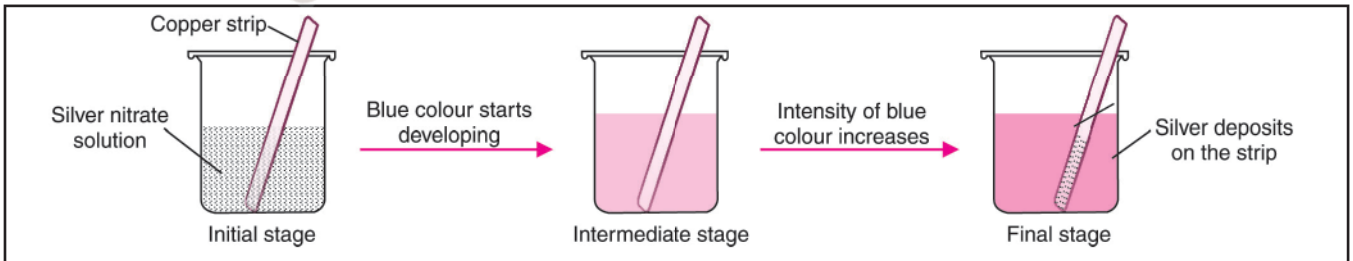

Fig. 2. Redox reaction between $AgNO_3$ and copper.

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Potassium permanganate is a strong oxidising agent in the presence of dil. H_2SO_4. In the presence of dil. H_2SO_4, it gives nascent oxygen which oxidises ferrous ammonium sulphate $[FeSO_4(NH_4)_2SO_4]$ to ferric sulphate as :

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$2FeSO_4(NH_4)_2SO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + 2(NH_4)_2SO_4 + H_2O] \times 5$$

$$2KMnO_4 + 10FeSO_4(NH_4)_2SO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 10(NH_4)_2SO_4 + 8H_2O$$

The ionic equation for the reaction may be written as :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Similarly, acidified $KMnO_4$ oxidises oxalic acid ($C_2H_2O_4$) solution. In this reaction, acidified $KMnO_4$ liberates nascent oxygen which oxidises oxalic acid to carbon dioxide as:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$C_2H_2O_4 + O \longrightarrow 2CO_2 + H_2O] \times 5$$

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

The ionic equation for the reaction may be written as :

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

SOLVED EXAMPLES

❑ Example 1.

Identify the species undergoing oxidation and reduction in the following reaction : **N.C.E.R.T.**

(i) $H_2S(g) + Cl_2(g) \longrightarrow 2HCl\ (g) + S\ (s)$

(ii) $3Fe_3O_4(s) + 8Al(s) \longrightarrow 9Fe(s) + 4Al_2O_3(s)$

(iii) $2Na(s) + H_2(g) \longrightarrow 2NaH(s)$

Solution:

(i) H_2S is oxidised because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element hydrogen has been removed from H_2S).

Chlorine has been reduced because hydrogen is added to it.

In terms of electronic concept, we can say,

Loses electrons : oxidation

$$H_2S\ (g) + Cl_2(g) \longrightarrow 2HCl\ (g) + S(s)$$

gains electrons : reduction

(ii) Aluminium is oxidised because oxygen is added to it.

Ferrous ferric oxide (Fe_3O_4) is reduced because oxygen has been removed from it.

In terms of electronic concept :

loses electrons : oxidation

$$3Fe_3O_4\ (s) + 8Al(s) \longrightarrow 9Fe(s) + 4Al_2O_3(s)$$

gains electrons : reduction

(iii) In this case, sodium has been oxidised and hydrogen has been reduced. This becomes more clear in terms of electronic concept :

loses electron : oxidation

$$2Na(s) + H_2(g) \longrightarrow 2Na^+H^-(s)$$

gains electrons : reduction

NaH is ionic compound and exists as Na^+H^-.

❑ Example 2.

Identify the oxidant and reductant in the following reactions :

(a) $Zn\ (s) + \frac{1}{2}O_2\ (g) \longrightarrow ZnO\ (s)$

(b) $CH_4\ (g) + 4Cl_2\ (g) \longrightarrow CCl_4\ (g) + 4HCl\ (g)$

(c) $I_2\ (aq) + 2S_2O_3^{2-}\ (aq) \longrightarrow 2I^-\ (aq) + S_4O_6^{2-}\ (aq)$

(d) $Zn\ (s) + 2H^+\ (aq) \longrightarrow Zn^{2+}\ (aq) + H_2\ (g)$

Solution: *(a)* $Zn\ (s) + \frac{1}{2}O_2\ (g) \longrightarrow ZnO\ (s)$

In this reaction, zinc donates electrons to O to give zinc ions and oxide ions. Thus, Zn acts as reductant while oxygen acts as **oxidant**.

(b) $CH_4\ (g) + 4Cl_2\ (g) \longrightarrow CCl_4\ (g) + 4HCl\ (g)$

CH_4 is oxidised and acts as **reductant** while Cl_2 is reduced and acts as **oxidant.**

(c) $I_2\ (aq) + 2S_2O_3^{2-}\ (aq) \longrightarrow 2I^-\ (aq) + S_4O_6^{2-}\ (aq)$

I_2 gains electrons and is reduced. Therefore, it acts as **oxidant.** $S_2O_3^{2-}$ acts as **reductant.**

(d) $Zn\ (s) + 2H^+\ (aq) \longrightarrow Zn^{2+}\ (aq) + H_2\ (g)$

Zinc loses electrons and gets oxidised. Therefore, it acts as **reductant.** Hydrogen gets reduced and acts as an **oxidant.**

❑ Example 3.

Justify that the reaction :

$2Na(s) + H_2(g) \longrightarrow 2NaH\ (s)$ *is a redox reaction.* **N.C.E.R.T.**

Solution: Sodium hydride is an ionic compound and it exists as $Na^+\ H^-$.

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$$2Na + H_2 \longrightarrow 2Na^+H^-(s)$$

The reaction may be split up into two half reactions:

$Na(s)$	$\longrightarrow$	$Na^+ + e^-] \times 2$	Oxidation
$H_2(g) + 2e^-$	$\longrightarrow$	$2H^-$	Reduction
$2Na(s) + H_2(g)$	$\longrightarrow$	$2\ NaH$	

In this reaction, Na is oxidised to Na^+ and hydrogen is reduced from H_2 to $2H^-$ ion. Therefore, it is a redox reaction.

OXIDATION NUMBER

The concept of electron transfer can easily explain the redox reactions in case of ionic substances. However, we cannot easily explain the redox changes in terms of electron transfer in case of covalent compounds. Now-a-days, to understand oxidation-reduction reactions, systematically, scientists assign an *oxidation number* or *oxidation state* to each chemical species (ionic or covalent) according to a set of rules. The concept of oxidation number has been very useful in balancing of redox reactions. The **oxidation number** is defined as

the charge which an atom of the element has in its ion or appears to have when present in the combined state with other atoms.

Oxidation number also gives *the charge which an atom appears to have when all other atoms are removed from it as ions*. During the removal of atoms, the electrons on the atoms are counted according to the following two arbitrary rules :

(*i*) *Electrons shared between two like atoms are divided equally between the sharing atoms.* In case of hydrogen molecule, for example, the electron pair is equally shared between the two hydrogen atoms. Therefore, one electron is counted with each hydrogen atom as shown below :

$$H\cdot \,|\, \cdot H$$

Now, each hydrogen atom is having one electron while its nucleus has one proton. Therefore, there is no net charge on each atom of hydrogen. In other words, oxidation number of hydrogen in hydrogen molecule is zero.

(*ii*) *Electrons shared between two unlike atoms are counted with more electronegative atom.* For example, in hydrogen chloride molecule, chlorine is more electronegative than hydrogen. Therefore, the shared pair is counted towards chlorine atom as shown below :

$$H\,|\,:\ddot{\underset{\cdot\cdot}{Cl}}:$$

As a result of this, chlorine gets one extra electron and acquires a unit negative charge. Hence, oxidation number of chlorine is – 1. On the other hand, hydrogen atom without electron has a unit positive charge. Hence, oxidation number of hydrogen in hydrogen chloride is + 1.

The oxidation number is a **fictitious charge** in case of covalent species. The oxidation number can have positive, zero or negative values depending upon their state of combination.

Rules for the Determination of Oxidation Number of an Atom

The following general rules are used for the calculation of oxidation number of an atom in a molecule :

1. *The oxidation number of an element in the free or elementary state or in any of its allotropic forms is always zero.* For example, oxidation numbers of helium in He, hydrogen in H_2, oxygen in O_2 or O_3, iron in Fe, carbon in diamond, helium atom in He, bromine in Br_2, phosphorus in P_4, sulphur in S_8, are zero.
2. *The oxidation number of an element in a single (monoatomic) ion is the same as the charge on the ion.* For example, oxidation number of K^+ is +1, of Ca^{2+} is + 2, of Al^{3+} is +3. Similarly, the oxidation numbers of Cl^-, SO_4^{2-} and PO_4^{3-} are –1, –2 and –3 respectively.
3. *In binary compounds of metal and non-metal, the oxidation number of metal is always positive while that of the non-metal is negative.* For example, in NaCl, the oxidation number of sodium is +1 and that of chlorine is –1.
4. *In compounds formed by the combination of non-metallic atoms, the atom with higher electronegativity is given negative oxidation number.* For example, in HCl, the oxidation number of chlorine in HCl is –1 because of its high electronegativity.

Similarly, N is given an oxidation number of –3, when it is bonded to less electronegative atom as in NH_3 and NI_3, However, it is given an oxidation number of +3 when it is bonded to more electronegative atom as in NCl_3.

Note. Rules (3) and (4) are based on the fact that atoms having high electronegativity have a tendency to form negative ions (anions) while atoms having low electronegativity have great tendency to form positive ions (cations).

5. *In all compounds of hydrogen, the oxidation number of hydrogen is +1 except in hydrides of active metals such as LiH, NaH, KH, MgH_2, CaH_2, etc., where hydrogen has the oxidation number of –1.*
6. *The oxidation number of oxygen is –2 in most of the compounds. However, there are two exceptions. The first exception is* ***peroxides***

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and ***superoxides*** *in which oxygen atoms are directly linked to each other. In peroxides (e.g., H_2O_2, Na_2O_2), each oxygen atom is assigned an oxidation number of –1 and in superoxides (e.g., KO_2, RbO_2) each oxygen atom is assigned an oxidation number of –1/2. The second exception is found in compounds in which* ***oxygen is bonded to fluorine.*** *For example, in OF_2 (oxygen difluoride) the oxidation number of oxygen is +2 and in O_2F_2(dioxygen difluoride) the oxidation number of each oxygen is +1. This is because of the fact that fluorine being most electronegative element known has always an oxidation number of –1.*

7. *The most electronegative element, fluorine has oxidation number –1. For other halogens, the oxidation number is generally –1, but there are exceptions when these are bonded to a more electronegative halogen atom or oxygen.* For example, in HI, the oxidation number of I is –1 but in IF_5, it is +5 and in IF_7, it is +7.
8. **For neutral molecule,** *the sum of the oxidation numbers of all the atoms is equal to zero.* For example, in NH_3 the sum of the oxidation numbers of nitrogen atom and 3 hydrogen atoms is equal to zero.

   For a polyatomic ion, *the sum of the oxidation numbers of all the atoms is equal to charge on the ion.* For example, in SO_4^{2-} ion, the sum of the oxidation numbers of sulphur atom and 4 oxygen atoms must be equal to –2.

It may be noted that oxidation number is also frequently called as **oxidation state.** For example, in H_2O, the oxidation state of hydrogen is +1 and the oxidation state of oxygen is –2. Similarly, in CO_2, the oxidation number of carbon is +4, which is also its oxidation state and the oxidation number of oxygen is –2, which is also its oxidation state. This means that *oxidation number gives the oxidation state of an element in a compound.*

Procedure for calculation of oxidation numbers. By applying the above rules, we can calculate the oxidation numbers of elements in the molecules/ions by the following steps :

(*i*) Write down the formula of the given molecule/ion leaving some space between the atoms.

(*ii*) Write oxidation number on the top of each atom. In case of the atom whose oxidation number has to be calculated write x.

(*iii*) Beneath the formula, write down the total oxidation numbers of each element. For this purpose, multiply the oxidation numbers of each atom with the number of atoms of that kind in the molecule/ion. Write the product in a bracket.

(*iv*) Equate the sum of the oxidation numbers to zero for neutral molecule and equal to charge on the ion.

(*v*) Solve for the value of x.

SOLVED EXAMPLES

❑ Example 4.

Calculate the oxidation number of sulphur in the following molecules/ions :

(a) H_2S *(b)* H_2SO_3 *(c)* SO_4^{2-}
(d) $Na_2S_2O_3$ *(e)* $S_2O_7^{2-}$ *(f)* H_2SO_4
(g) $S_2O_4^{2-}$

Solution: (*a*) **H_2S.** The oxidation number of hydrogen is +1. Let the oxidation number of sulphur be x.

+1	x	
H_2	S	
(1×2)	(x)	
$1 \times 2 + x = 0$	$\therefore$	$x = -2$

Oxidation number of S in H_2S is **–2.**

(*b*) **H_2SO_3.** Oxidation number of hydrogen is +1 and that of oxygen is –2. Let the oxidation number of S be x.

+1	x	–2
H_2	S	O_3
$(+1 \times 2)$	x	(-2×3)

$$(+1 \times 2) + x + (-2 \times 3) = 0$$
or $$+2 + x - 6 = 0$$
or $$x = +4$$

Oxidation number of S in H_2SO_3 is **+ 4.**

(*c*) **SO_4^{2-}.** The oxidation number of oxygen is –2 and let the oxidation number of S be x.

$$\begin{bmatrix} x & -2 \\ S & O_4 \end{bmatrix}^{2-}$$

x (-2×4)

$x + (-2 \times 4) = -2$ or $x = -2 + 8$

or $x = +6$

Oxidation number of S in SO_4^{2-} is **+6.**

(*d*) **$Na_2S_2O_3$.** The oxidation number of Na is +1 and that of oxygen is –2. Let the oxidation number of S be x.

+1	x	–2
Na_2	S_2	O_3
$(+1 \times 2)$	$(x \times 2)$	(-2×3)

$$(+1 \times 2) + (x \times 2) + (-2 \times 3) = 0$$
$$+ 2 + 2x - 6 = 0 \quad \text{or} \quad 2x = 4$$
$$x = +2$$

Oxidation number of S in $Na_2S_2O_3$ is **+2.**

(*e*) **$S_2O_7^{2-}$.** The oxidation number of oxygen is –2 and let the oxidation number of sulphur be x.

$$\begin{bmatrix} x & -2 \\ S_2 & O_7 \end{bmatrix}^{2-}$$

$(x \times 2)$ (-2×7)

$$x \times 2 + (-2 \times 7) = -2$$
$$2x = -2 + 14$$
$$\therefore \quad x = 6$$

Oxidation number of S in $S_2O_7^{2-}$ is **+ 6.**

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(*f*) **H_2SO_4.** The oxidation number of hydrogen is +1 and that of oxygen is –2. Let the oxidation number of S be x

+1	x	–2
H_2	S	O_4
$(+1 \times 2)$	x	(-2×4)

$$(+1 \times 2) + x + (-2 \times 4) = 0$$

or $$+2 + x - 8 = 0$$

or $$x = +\mathbf{6}$$

Oxidation number of S in H_2SO_4 is **+ 6.**

(*g*) **$S_2O_4^{2-}$.** The oxidation number of oxygen is –2 and let the oxidation number of sulphur be x.

$$\begin{bmatrix} x & -2 \\ S_2 & O_4 \end{bmatrix}^{2-}$$

$$(x \times 2)\ (-2 \times 4)$$

$$x \times 2 + (-2 \times 4) = -2$$

$$2x - 8 = -2 \quad \therefore x = +3$$

$\therefore$ Oxidation number of S in $S_2O_4^{2-}$ is **+3.**

❑ Example 5.

What is the oxidation number of the underlined atoms in each of the following molecules / ions ?

(a) $\underline{Cl}O_3^-$ *(b)* $\underline{Br}F_3$ *(c)* $\underline{C}H_4$ *(d)* $\underline{C_6}H_{12}O_6$ *(e)* $Na_2\underline{B_4}O_7$ *(f)* $Na_4[\underline{Fe}(CN)_6]$ *(g)* $\underline{N_2}H_4$.

Solution: Suppose x be the oxidation number of the underlined atom :

(*a*) ClO_3^- $\quad x + (-2 \times 3) = -1$

$x - 6 = -1$ or $x = +5$

(*b*) BrF_3 $\quad x + (-1 \times 3) = 0$

$x - 3 = 0$ or $x = +3$

(*c*) CH_4 $\quad x + (1 \times 4) = 0$

$x + 4 = 0$ or $x = -4$

(*d*) $C_6H_{12}O_6$ $\quad 6 \times x + 1 \times 12 + (-2 \times 6) = 0$

$6x + 12 - 12 = 0$ or $x = 0$

(*e*) $Na_2B_4O_7$ $\quad (+1 \times 2) + (x \times 4) + (-2 \times 7) = 0$

$+2 + 4x - 14 = 0$ or $x = +3$

(*f*) $Na_4[Fe(CN)_6]$ $\quad (+1 \times 4) + x + (-1 \times 6) = 0$

$+4 + x - 6 =$ or $x = +2$

(*g*) N_2H_4 $\quad 2 \times x + (1 \times 4) = 0$

$2x + 4 = 0$ or $x = -2$

❑ Example 6.

Calculate the oxidation number of (i) Fe in Fe_3O_4 (ii) S in $Na_2S_4O_6$ (iii) Pb in Pb_3O_4 (iv) N in $(NH_4)_2SO_4$.

Solution:

(*i*) **Fe in Fe_3O_4.** Let the oxidation number of Fe be x.

x	–2	$3x - 8 = 0$
Fe_3	O_4	$3x = 8$
$(x \times 3)$	(-2×4)	$x = 8/3 =$ **2.67**

(*ii*) **S in $Na_2S_4O_6$.** Let the oxidation number of S be x.

+1	x	–2	$2 + 4x - 12 = 0$
Na_2	S_4	O_6	$4x = 10$
$(+1 \times 2)$	$(x \times 4)$	(-2×6)	$x = \frac{10}{4} =$ **2.5**

(*iii*) **Pb in Pb_3O_4.** Let the oxidation no. of Pb be x.

x	–2	$3x - 8 = 0$
Pb_3	O_4	$3x = 8$
$(x \times 3)$	(-2×4)	or $x = \frac{8}{3} =$ **2.67**

(*iv*) **N in $(NH_4)_2SO_4$.** Let the oxidation no. of N be x.

$\left(\overset{x\ +1}{NH_4}\right)_2 SO_4^{2-}$ $\quad 2x + 2\,(+1 \times 4) + (-2) = 0$

$2x + 6 = 0$

$\therefore$ $\quad 2x = -6$ or $x = -\frac{6}{2} = \mathbf{-3}$

KEY NOTE

PARADOX OF FRACTIONAL OXIDATION NUMBER

▶ For some compounds, the general rules give *fractional oxidation number* to some atoms. For example, the oxidation number of Fe in Fe_3O_4 comes out to be $+\frac{8}{3}$. This is **strange** because electrons are never shared or transferred in fractions.

Actually, this fractional oxidation number is the **average** oxidation number of the element in the compound. This can be explained by the fact that Fe_3O_4 contains Fe atoms of both + 2 and + 3 oxidation number. It is a stoichiometric mixture of ferrous (FeO) and ferric (Fe_2O_3) oxides combined as FeO . Fe_2O_3. Therefore, the oxidation number found in such cases is **average oxidation number.**

Similarly, Mn_3O_4 is regarded as a mixture of MnO and MnO_2 having the composition $2MnO \cdot MnO_2$. Therefore, the oxidation number of Mn in MnO is +2 and that in MnO_2 is +4. Hence, average comes out to be $[2(+2) + 1(+4)]/3 = 8/3$.

Red lead, Pb_3O_4 is regarded as a mixture with composition of $2PbO \cdot PbO_2$. In PbO, the oxidation number of Pb is +2 while in PbO_2, the oxidation number of Pb is +4. The average value is $[2(+2) + 1(+4)]/3 = 8/3$.

Similarly, in ferriferrocyanide, $Fe_4[Fe(CN)_6]_3$ molecule, there are four iron atoms with oxidation number + 3 and three iron atoms with oxidation number + 2. The oxidation number of iron in this molecule is the average of all these atoms equal to 18/7 (strange number). Thus, *the average oxidation number indicates average of atoms in different bonding situations in a compound.*

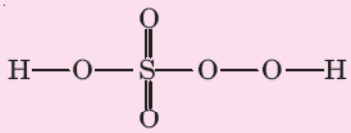
▶ In some compounds, the knowledge of chemical bonds or structures is essential to calculate oxidation numbers. For example,

(*a*) **Caro's acid, H_2SO_5 (peroxymonosulphuric acid)**

The O.N. can be calculated as

$2 \times (+1) + x + 5(-2) = 0$, $x = +8$

But this is wrong because the maximum oxidation number of S cannot be more than +6 because it has only six electrons in its valence shell. In this structure, two oxygen atoms are bonded by a peroxide bond as



In the peroxide bond each O atom has –1 oxidation state

$H_2S(O_2)O_3$

$2(+1) + x + 2(-1) + 3(-2) = 0$ or $x - 6 = 0$

$\therefore$ $x = +6$

$\therefore$ O.N. of S in H_2SO_5 is +6

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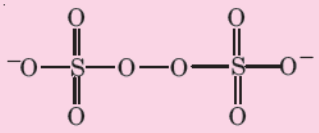
Similarly in $S_2O_8^{2-}$ ion,



There is one peroxide bond

$S_2(O_2)O_6^{2-}$ $2x + 2(-1) + 6(-2) = -2$ or $2x = 12$ or $x = +6$

(*b*) **Oxidation number of Cr in CrO_5**

By conventional method

CrO_5 $x + 5(-2) = 0$ $\therefore$ $x = +10$

But this is wrong because maximum O.N. of Cr is +6 ($3d^5 4s^1$) because it has six electrons in its valence shell. The structure of CrO_5 is

It contains two peroxide bonds and may be written as $Cr(O_2)_2O$

O.N. can be calculated as

x + $1 \times (-2)$ + $4(-1) = 0$

(for Cr) (for one O) (for O–O bond)

or $x - 2 - 4 = 0$

$\therefore$ $x = +6$

(*c*) **Oxidation number of Cl in bleaching powder, $CaOCl_2$**

Average O.N. of Cl in $CaOCl_2$ is

$+2 - 2 + 2x = 0$

$\therefore$ $x = 0$

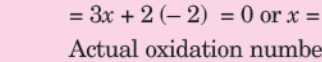
However, it may be noted that the composition of bleaching powder is $Ca^{2+}(OCl^-)Cl^-$. In this O.N. of Cl in OCl^- is + 1 and in Cl^- is – 1 and the average of two oxidation numbers $1 \times (+1) + 1 \times (-1) = 0$

(*d*) **C_3O_2 (Carbon suboxide)**

Calculated oxidation number of C

$= 3x + 2(-2) = 0$ or $x = \frac{4}{3}$

Actual oxidation numbers of different C atoms are :



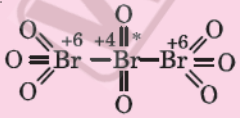
(the element marked with asterisk (*) shows different oxidation number from rest of the atoms of the same element).

(*e*) **Br_3O_8 (tribromooctaoxide)**

Calculated oxidation number of Br

$= 3x + 8(-2) = 0$ or $x = \frac{16}{3}$

Actual oxidation number of different Br atoms are :

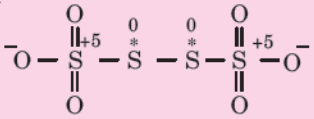


(*f*) **$S_4O_6^{2-}$ (tetrathionate ion)**

Calculated oxidation number of S

$= 4x + 6(-2) = -2$ or $x = +\frac{5}{2}$

Actual oxidation number of different S atoms are:



(*g*) **HNO_4 (peroxynitric acid)**

The oxidation number of N comes out to be +7. This is **not possible for N.** In fact, HNO_4 is peroxynitric acid which contains one peroxide group $[-O-O-]^{2-}$. The formula may be written as $HNO_2(O_2)$. In this case, the oxidation number comes out to be $(+1 + x - 4 - 2 = 0$ or $x = +5) + 5$.

SOLVED EXAMPLES

❑ Example 7.

Calculate the oxidation number of carbon in the following compounds :

C_2H_2, CO_2, C_2H_6, CH_3OH, $HCOOH$, CH_2O.

Solution: In all these compounds, the O.N. (oxidation number) of oxygen is –2 and that of hydrogen is +1. So, oxidation number of carbon assuming x can be easily calculated as :

C_2H_2	: $2x + 2 \times 1 = 0$	$2x = -2$	$\therefore$ $x = -1$
CO_2	: $x - (2 \times 2) = 0$		$\therefore$ $x = +4$
C_2H_6	: $2x + (1 \times 6) = 0$	$2x = -6$	$\therefore$ $x = -3$
CH_3OH	: $x + (1 \times 4) - 2$		$\therefore$ $x = -2$
$HCOOH$	: $x + (2 \times 1) + (-2 \times 2) = 0$	$x - 2 = 0$	$\therefore$ $x = +2$
CH_2O	: $x + (1 \times 2) + (-2) = 0$		$\therefore$ $x = 0$

❑ Example 8.

Give examples of substances where carbon can exhibit oxidation states from –4 to + 4 and nitrogen from –3 to +5.

Solution:

Carbon	Nitrogen
–4 CH_4	–3 NH_3
–3 C_2H_6	–2 N_2H_4
–2 C_2H_4	–1 N_2H_2
–1 C_2H_2	0 N_2
0 $C_6H_{12}O_6$	+1 N_2O
+2 CO	+2 NO
	+3 N_2O_3
+4 CO_2	+4 NO_2
	+5 N_2O_5

❑ Example 9.

Calculate the oxidation number of all the atoms in the following compounds and ions : **N.C.E.R.T.**

CO_2, SiO_2, $PbSO_4$, ClO_4^-

Solution: CO_2 : Oxidation number of each oxygen atom = –2

Oxidation number of carbon (say x)

x	–2
C	O_2

$x + (-2 \times 2) = 0$ or $x = +4$

$\therefore$ Oxidation number of C = +4, O = –2

SiO_2 : Oxidation number of each oxygen atom = –2

Oxidation number of silicon (say x)

x	–2
Si	O_2

$x + (-2 \times 2) = 0$ or $x = +4$

Oxidation number of Si = + 4, O = – 2

$PbSO_4$: Oxidation number of each oxygen = –2

Oxidation number of lead (Pb) = +2

Oxidation number of sulphur (say x)

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$$\begin{matrix} +2 & x & -2 \\ Pb & S & O_4 \end{matrix}$$

$+2 + x + (-2 \times 4) = 0$ or $x = +6$

Oxidation number of Pb = + 2, S = + 6, O = – 2

ClO_4^- : Oxidation number of each oxygen = –2

Oxidation number of chlorine (say x)

$$\begin{bmatrix} x & -2 \\ Cl & O_4 \end{bmatrix}^-$$

$x + (-2 \times 4) = -1$ or $x = +7$

∴ Oxidation number of O = 2, Cl = **+7**

❑ **Example 10.**

Calculate the oxidation number of sulphur in $S_2O_8^{2-}$ ion.

Solution: In $S_2O_8^{2-}$, there is one peroxide bond (—O—O—) therefore, two oxygen atoms, oxidation number is – 1 (*i.e.*, O_2^{2-}) and for the other six oxygen atoms, the oxidation number is – 2.

$S_2O_8^{2-}$

$2x + (-2 \times 6) + (-1 \times 2) = -2$

$2x = -2 + 14 = +12$

∴ x = **+6.**

Thus, by the application of rules, we can calculate the oxidation number of the desired element in a compound or in an ion. Metals have positive oxidation states while non-metals may have positive or negative oxidation states. The atoms of transition elements (*d*-block elements) usually exhibit several oxidation states. The highest positive oxidation state of a representative element is the group number for the first two groups (*s*-block elements) and the group number minus 10 for other groups, *i.e. p*-block elements (except for noble gases). Thus, the highest value of oxidation state exhibited by an atom of an element generally increases across period in the periodic table. For example, in the third period, the highest value of oxidation state increases from +1 to +7 in the compounds of the elements, as shown below :

	s-block		*p*-block				
Group	1	2	13	14	15	16	17
Element	Na	Mg	Al	Si	P	S	Cl
Compound	NaCl	$MgSO_4$	AlF_3	$SiCl_4$	PF_5, P_4O_{10}	SF_6, SO_3	$HClO_4$
Oxidation state of the group element in the compound	+1	+2	+3	+4	+5	+6	+7

Practice Problems

◑ **1.** What is the oxidation number of nitrogen in (*a*) nitric acid (*b*) nitrous acid (*c*) nitric oxide (*d*) nitrous oxide (*e*) ammonia (*f*) N_2

◑ **2.** What is the oxidation number of the underlined atoms in the following ?
$K\underline{Mn}O_4$, $Na_2\underline{Cr}_2O_7$, $\underline{Fe}_3O_4$, $K\underline{Cl}O_3$, $\underline{P}O_4^{3-}$, $\underline{C}Cl_4$

◑ **3.** What are the oxidation numbers of the following ?
(*a*) Cr in CrO_4^{2-} (*b*) C in $C_6H_{12}O_6$
(*c*) I in IF_7 (*d*) O in O_3

◑ **4.** Determine the oxidation number of the atom in bold in the following species :
BH_3, BF_3, **Br**O_4^-, HPO_4^{2-}, **S_2**O_3^{2-}, **Si**H_4

◑ **5.** Determine the oxidation number of Cl in HCl, HClO, ClO_4^- and Ca(OCl) Cl and ClO_2.

◑ **6.** Calculate the oxidation number of all the atoms in the following well known oxidants :
$KMnO_4$, $K_2Cr_2O_7$, $KClO_4$

◑ **7.** Calculate the oxidation number of oxygen in the following : OF_2, O_2, Na_2O_2 and CH_3COOH

◑ **8.** Calculate the oxidation number of C in the following : C_2H_6, C_4H_{10}, CO, CO_2 and HCO_3^-

Answers to Practice Problems

◐ **1.** (*a*) +5, (*b*) +3, (*c*) +2, (*d*) +1, (*e*) –3; nitrogen is more electronegative than H, (*f*) 0.

◐ **2.** +7, +6, +2.66, + 5, + 5, + 4 (Cl is more electronegative than C)

◐ **3.** (a) + 6, (b) 0, (c) + 7, (d) 0

◐ **4.** –3, + 3, + 7, + 5, + 2, – 4

◐ **5.** –1, +1, +7, 0 ($+2 -2 -2x = 0 \therefore x = 0$) + 4

◐ **6.** K(+1), Mn(+7), O(–2), K(+1), Cr(+6), O(–2), K(+1), Cl (+7), O(–2)

◐ **7.** + 2, 0, – 1, – 1

◐ **8.** –3, –2.5, + 2, +4 and +4

REDOX REACTIONS IN TERMS OF OXIDATION NUMBER

Based upon the concept of oxidation number, **oxidation** is

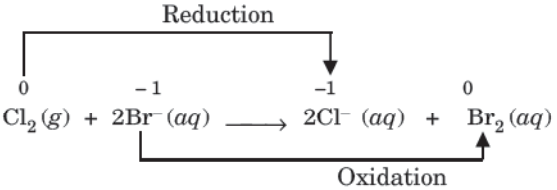
a chemical change in which there is an increase in oxidation number.

On the other hand, **reduction** is

a chemical change in which there is a decrease in the oxidation number.

For example, consider the following reactions:

(*i*)



Here oxidation number of bromine increases from –1 to 0 and that of chlorine decreases from 0 to –1. Therefore, bromide ion is oxidised to Br_2 and Cl_2 is reduced to Cl^- ions.

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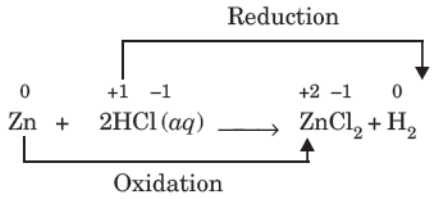
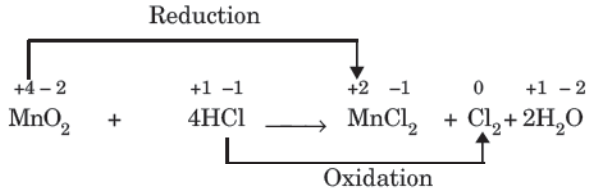
(*ii*)



In this reaction, oxidation number of zinc increases from 0 to +2 and therefore zinc is oxidised. The oxidation number of hydrogen decreases from +1 to 0 and therefore, H_2 is reduced. The oxidation number of chlorine remains unchanged.

(*iii*)



In this reaction, the oxidation number of manganese decreases from +4 (in MnO_2) to +2 (in $MnCl_2$) indicating that manganese dioxide undergoes reduction. On the other hand, the oxidation number of chlorine increases from –1 (in HCl) to 0 (in Cl_2) indicating that hydrochloric acid undergoes oxidation.

Similarly, oxidising and reducing agents can be defined as follows :

Oxidising agent is

a substance which increases the oxidation number of other substance in a chemical reaction.

Alternatively, **the oxidation number of oxidising agent decreases**. On the other hand, **reducing agent**

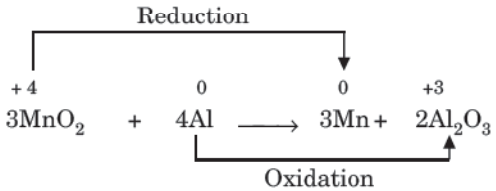
is a substance which decreases the oxidation number of other substance in a chemical reaction.

Thus, the **oxidation number of a reducing agent increases**.

TO SUM UP:

An increase in oxidation number corresponds to oxidation of the element in the given compound that acts as a reductant or reducing agent. A decrease in oxidation number corresponds to reduction of the element in a compound and it behaves as an oxidant or oxidising agent.

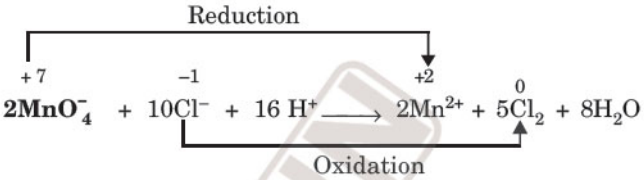
In the above example (*iii*), manganese dioxide acts as an oxidising agent (oxidation number of Mn decreases from +4 to +2) while hydrochloric acid acts as a reducing agent (oxidation number of Cl increases from –1 to 0). Similarly, consider the reaction :



(Oxidation numbers of only those atoms are shown which undergo change).

In this case, MnO_2 is reduced (oxidation number of Mn decreases from +4 to 0) and Al is oxidised (oxidation number increases from 0 to +3). Thus, Al acts as a reducing agent and MnO_2 acts as an oxidising agent.

Consider an ionic reaction :



In this case, MnO^-_4 is reduced (oxidation number of Mn decreases from +7 to +2) and Cl is oxidised (oxidation number increases from –1 to 0). Thus MnO_4^- acts as an oxidising agent and Cl^- acts as a reducing agent.

The various terms studied in this chapter can be summed up as :

Oxidation	:	Loss of electrons or Increase in oxidation number.
Reduction	:	Gain of electrons or Decrease in oxidation number.
Oxidising agent	:	Electron acceptor : Substance whose oxidation number decreases.
Reducing agent	:	Electron donor : Substance whose oxidation number increases.

SOLVED EXAMPLES

Example 11.

Identify the oxidising and reducing agent and the atoms undergoing oxidation and reduction in the following reactions :

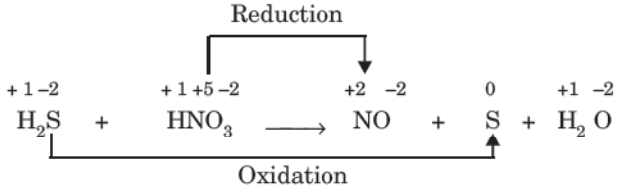
(*a*) $H_2S + HNO_3 \longrightarrow NO + S + H_2O$

(*b*) $Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$

(*c*) $I_2\,(g) + H_2S\,(g) \longrightarrow 2HI\,(g) + S(s)$

(*d*) $4Zn\,(s) + 10H^+\,(aq) + NO_3^-\,(aq) \longrightarrow 4Zn^{2+}\,(aq) + NH_4^+(aq) + 3H_2O(l)$

Solution: (*a*)



We observe that oxidation number of S increases from –2 (in H_2S) to 0 (in S) which means that H_2S is being oxidised or H_2S is acting as a reductant. The oxidation number of nitrogen decreases from +5 (in HNO_3) to +2 in (NO) indicating that HNO_3 is being reduced or HNO_3 is acting as an oxidant.

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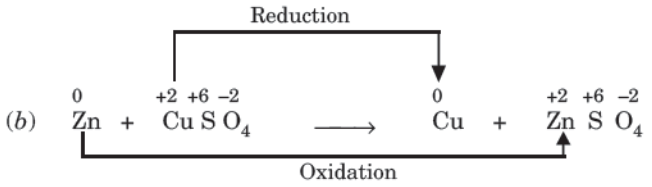
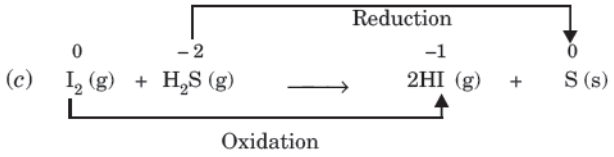
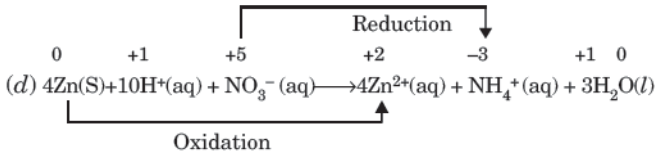


We observe that oxidation number of zinc increases from 0 (in Zn) to +2 (in $ZnSO_4$) which means that Zn is being oxidised or zinc is acting as a reducant. On the other hand, the oxidation number of copper decreases from +2 (in $CuSO_4$) to 0 (in Cu), indicating that copper is being reduced or $CuSO_4$ is acting as an oxidant.



Oxidation number of iodine decreases from 0 to –1. Therefore, it is reduced and acts as an oxidant. The oxidation number of S in hydrogen sulphide increases from –2 to 0. Therefore, it is oxidised and hence acts as a **reductant**.



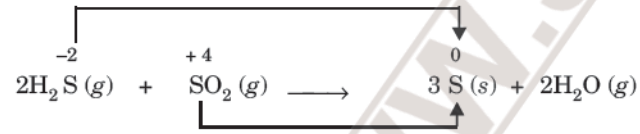
Oxidation number of zinc increases from 0 to +2. Therefore, it is oxidised and acts as a reductant. The oxidation number of N decreases from +5 to –3. and, therefore, it is reduced and acts as an **oxidant**.

❑ Example 12.

Determine the change in the oxidation number of S in H_2S and SO_2 in the following industrial reaction:

$$2H_2S\,(g) + SO_2\,(g) \longrightarrow 3S\,(s) + 2H_2O\,(g)$$

Solution:



Change in O.N. of S in H_2S from – 2 to 0

Change in O.N. of S in SO_2 from + 4 to 0.

❑ Example 13.

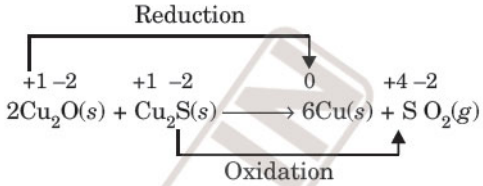
Justify that the reaction :

$$2Cu_2O(s) + Cu_2S(s) \longrightarrow 6Cu\,(s) + SO_2(g)$$

is a redox reaction. Identify the species oxidised, reduced, acts as an oxidant or a reductant.

Solution: ***N.C.E.R.T.***

Let us write the oxidation number of each element :



In this reaction copper is **reduced** from +1 state (in Cu_2O or Cu_2S) to 0 (in Cu) whereas sulphur is **oxidised** from –2 state (in Cu_2S) to +4 (in SO_2). Therefore, the above reaction is a redox reaction.

In the reaction, Cu_2O helps sulphur in Cu_2S to increase its oxidation number from –2 to +4 and therefore, **Cu_2O is oxidant**.

Alternatively, sulphur in Cu_2S helps copper in both Cu_2O and Cu_2S to decrease its oxidation number (i.e., get reduced) and therefore, **Cu_2S is reductant**.

Practice Problems

9. Identify the oxidants and reductants in the following reactions :

(*a*) $CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 2HCl\,(g)$

(*b*) $C_2H_2O_4(aq) + 2H^+ + MnO_2(s) \longrightarrow Mn^{2+}(aq) + 2CO_2\,(g) + 2H_2O\,(l)$

(*c*) $I_2(aq) + S_2O_3{}^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6{}^{2-}(aq)$

(*d*) $Cl_2\,(g) + 2Br^-\,(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$

Answers to Practice Problems

9. Oxidants and reductant are respectively

(*a*) Cl_2, CH_4, (*b*) MnO_2, $C_2H_2O_4$, (*c*) I_2, $S_2O_3{}^{2-}$, (*d*) Cl_2, Br^-.

Oxidation Number and Valency

There have been confusion regarding the usage of the terms oxidation number and valency. The two terms have different meanings as discussed below :

Valency	Oxidation number
1. Valency is the combining capacity of an atom. It is expressed as the number of hydrogen atoms or double the number of oxygen atoms with which an atom of the element combines.	1. Oxidation number is the residual charge which an atom has or appears to have when all the atoms are removed as ions.
2. Since it refers to combining capacity, it is a whole number only. As such it does not carry any plus or minus sign. For example, in NH_3 the valency of nitrogen is 3 and that of hydrogen is 1.	2. Since it refers to charge, it can be positive, negative or zero. For example, in NH_3, nitrogen has oxidation number of –3 and that of hydrogen is +1.
3. Valency of an element cannot be zero (except for noble gases).	3. Oxidation number of an element can be zero. For example, oxidation number of C in CH_2Cl_2 is zero.
4. Since atoms always combine in whole numbers, valency of an element is always a whole number.	4. Oxidation number may have fractional values. For example, oxidation number of S in $Na_2S_4O_6$ is +2.5.
5. In general, elements like C, N and S exhibit constant valency. Thus, valency of N in all its compounds is three.	5. Even the elements C, N and S exhibit variable valency. For example, the oxidation number of N (given in brackets) in its compounds vary from +5 to –3 as: N_2O_5(+5), NO_2(+4), N_2O_3(+3), NO(+2), N_2O(+1), N_2(0), N_2H_4(–2) and NH_3(–3)

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OXIDATION NUMBER AND NOMENCLATURE

When an element forms two monoatomic cations (representing different oxidation states), the two ions are distinguished by using the ending *-ous* and *ic*. The suffix **-ous** is used for the cation with lower oxidation state and the suffix **-ic** is used for the cation with higher oxidation state. For example,

Cu^+ (oxidation number +1) cuprous : Cu^{2+} (oxidation number +2) cupric.

However, Albert Stock proposed a new system known as **Stock system.** In this system, the oxidation states are indicated by Roman numeral written in parentheses immediately after the name of the element. For example,

Cu_2O	:	Copper (I) oxide
SnO	:	Tin (II) oxide
$FeCl_2$	:	Iron (II) chloride
$FeCl_3$	:	Iron (III) chloride
CuO	:	Copper (II) oxide
SnO_2	:	Tin (IV) oxide
AuCl	:	Gold (I) chloride
$AuCl_3$	:	Gold (III) chloride
Hg_2Cl_2	:	Mercury (I) chloride
$HgCl_2$	:	Mercury (II) chloride

Many more examples are taken for illustration :

Mn_2O_7	:	Manganese (VII) oxide
$K_2Cr_2O_7$	:	Potassium dichromate (VI)
Na_2CrO_4	:	Sodium chromate (VI)
V_2O_5	:	Vanadium (V) oxide

Stock system is not used for non-metals.

SOLVED EXAMPLES

❑ Example 14.

Write formulas for the following compounds

(i) Mercury(II) chloride (ii) Nickel (II) sulphate

(iii) Tin(IV) oxide (iv) Thallium (I) sulphate

(v) Iron (III) sulphate (vi) Chromium (III) oxide.

Solution: *N.C.E.R.T.*

(*i*) $HgCl_2$ (*ii*) $NiSO_4$ (*iii*) SnO_2

(*iv*) Tl_2SO_4 (*v*) $Fe_2(SO_4)_3$ (*vi*) Cr_2O_3

❑ Example 15.

Using stock notation, represent the following compounds :

(i) $HAuCl_4$ *(ii)* Tl_2O *(iii)* FeO *(iv)* Fe_2O_3

(v) CuI *(vi)* CuO *(vii)* MnO *(viii)* MnO_2

N.C.E.R.T.

Solution:

Knowing oxidation of metallic element, these compounds may be represented as :

(*i*) $\overset{+3}{H}AuCl_4$: HAu(III)Cl_4

(*ii*) $\overset{+1}{Tl_2}O$: Tl_2(I)O

(*iii*) $\overset{+2}{Fe}O$: Fe(II)O

(*iv*) $\overset{+3}{Fe_2}O_3$: Fe_2(III)O_3

(*v*) $\overset{+1}{Cu}I$: Cu(I)I

(*vi*) $\overset{+2}{Cu}O$: Cu(II)O

(*vii*) $\overset{+2}{Mn}O$: Mn(II)O

(*viii*) $\overset{+4}{Mn}O_2$: Mn(IV)O_2

TYPES OF REDOX REACTIONS

The redox reactions may be classified into the following types :

1. Combination reactions

The chemical reactions in which two or more substances (elements or compounds) combine to form a single substance are called **combination reactions.** A combination reaction may be expressed as :

$$A + B \longrightarrow C$$

For a combination reaction to be a redox reaction one or both A and B must be in the elementary form.

All combustion reactions in which elemental oxygen is used and all other reactions which involve elements other than oxygen are redox reactions.

Some common combination redox reactions are :

$$\overset{0}{C}(s) + \overset{0}{O_2}(g) \longrightarrow \overset{+4\ -2}{C\,O_2}$$

$$\overset{-4\ +1}{CH_4}(g) + 2\overset{0}{O_2}(g) \longrightarrow \overset{+4\ -2}{C\,O_2}(g) + 2\overset{+1\ -2}{H_2\,O}(l)$$

$$2\overset{0}{Mg}(s) + \overset{0}{O_2}(g) \longrightarrow 2\overset{+2\ -2}{MgO}(s)$$

$$3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \longrightarrow \overset{+2\ -3}{Mg_3N_2}(s)$$

$$\overset{0}{Fe}(s) + \overset{0}{S}(s) \longrightarrow \overset{+2-2}{FeS}(s)$$

2. Decomposition reactions

The chemical reactions in which a compound breaks up into two or more simpler substances are called **decomposition reactions.** The decomposition reactions are the opposite of combination reactions. For a decomposition reaction to be a redox reaction, at least one of the component formed after the break down of the compound must be in the elemental state.

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Some common examples of redox decomposition reactions are :

$$\overset{+1\ -2}{2H_2O\,(l)} \xrightarrow{\text{Heat}} \overset{0}{2H_2(g)} + \overset{0}{O_2(g)}$$

$$\overset{+1\ -1}{2NaH\,(s)} \xrightarrow{\text{Heat}} \overset{0}{2Na(s)} + \overset{0}{H_2(g)}$$

$$\overset{+2\ -2}{2HgO\,(s)} \xrightarrow{\text{Heat}} \overset{0}{2Hg(l)} + \overset{0}{O_2(g)}$$

$$\overset{+1\ +5\ -2}{2KClO_3(s)} \xrightarrow{\text{Heat}} \overset{+1\ -1}{2KCl(s)} + \overset{0}{3O_2(g)}$$

It may be noted that all decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction because it does not involve change in oxidation number of elements.

$$\overset{+2\ +4-2}{CaCO_3(s)} \xrightarrow{\text{Heat}} \overset{+2\ -2}{CaO(s)} + \overset{+4\ -2}{C\ O_2(g)}$$

3. Displacement reactions

The reactions in which one ion (or atom) in a compound is replaced by an ion (or atom) of other element are called **displacement reactions.** These reactions are very common in chemistry in which a more active metal displaces or removes another atom from a compound. In general, a displacement reaction may be expressed as :

$$XY + Z \longrightarrow X + ZY$$

In this reaction, the atom X from the compound XY has been displaced by another atom Z.

The displacement reactions are of two types :

(*a*) *Metal displacement* and

(*b*) *Non-metal displacement*

(*a*) Metal displacement reactions. In these reactions, a metal in a compound can be displaced by another metal in the uncombined state. These have already been discussed earlier.

Some common examples of metal displacement reactions are :

$$\overset{+2\ +6\ -2}{CuSO_4(aq)} + \overset{0}{Zn(s)} \longrightarrow \overset{0}{Cu(s)} + \overset{+2+6-2}{ZnSO_4(aq)}$$

$$\overset{+2\ +6\ -2}{NiSO_4(aq)} + \overset{0}{2Co(s)} \longrightarrow \overset{+2+6-2}{CoSO_4(s)} + \overset{0}{Ni(s)}$$

$$\overset{+3\ -2}{Fe_2O_3(s)} + \overset{0}{Al(s)} \longrightarrow \overset{0}{2Fe(s)} + \overset{+3\ -2}{Al_2O_3(s)}$$

$$\overset{+3\ -2}{Cr_2O_3(s)} + \overset{0}{2Al(s)} \xrightarrow{\text{Heat}} \overset{+3\ -2}{Al_2O_3(s)} + \overset{0}{2Cr(s)}$$

$$\overset{+4\ -1}{TiCl_4(l)} + \overset{0}{2Mg(s)} \xrightarrow{\text{Heat}} \overset{0}{Ti(s)} + \overset{+2\ -1}{2MgCl_2(s)}$$

$$\overset{+5\ -2}{V_2O_5(s)} + \overset{0}{5Ca(s)} \xrightarrow{\text{Heat}} \overset{0}{2V(s)} + \overset{+2\ -2}{5CaO(s)}$$

In each of these reactions, the reducing metal is a better reducing agent than the metal being reduced (*e.g.,* Cu, Ni, Fe, Cr, Ti, V, etc.). This is because the reducing metal has greater tendency to lose electrons as compared to the one which is reduced.

(*b*) Non-Metal displacement reactions. The non-metal displacement redox reactions are mainly hydrogen displacement or oxygen displacement reactions. For example,

(*i*) All alkali metals and some alkaline earth metals (*e.g,* Ca, Sr, Ba) which are good reducing agents will displace hydrogen from cold water.

$$\overset{0}{2Na(s)} + \overset{+1\ -2}{2H_2O(l)} \longrightarrow \overset{+1\ -2+1}{2NaOH(aq)} + \overset{0}{H_2(g)}$$

$$\overset{0}{Mg(s)} + \overset{+1\ -2}{2H_2O(l)} \longrightarrow \overset{+2\ -2+1}{Mg(OH)_2(s)} + \overset{0}{H_2(g)}$$

$$\overset{0}{Ca\ (s)} + \overset{+1\ -2}{2H_2O(l)} \longrightarrow \overset{+2-2+1}{Ca(OH)_2(aq)} + \overset{+0}{H_2(g)}$$

(*ii*) Less active metals such as magnesium and iron react with steam to produce dihydrogen gas.

$$\overset{0}{Mg(s)} + \underset{\text{(Steam)}}{\overset{+1\ -2}{2H_2O(g)}} \xrightarrow{\text{Heat}} \overset{+2\ -2+1}{Mg(OH)_2} + \overset{0}{H_2(g)}$$

$$\overset{0}{2\ Fe(s)} + \overset{+1-2}{3H_2O(l)} \xrightarrow{\text{Heat}} \overset{+3\ -2}{Fe_2O_3} + \overset{0}{3H_2(g)}$$

(*iii*) Many metals including those which donot react with cold water displace hydrogen from acids.

For example,

$$\overset{0}{Zn(s)} + \overset{+1-1}{HCl\ (aq)} \longrightarrow \overset{+2-1}{ZnCl_2(aq)} + \overset{0}{H_2(g)}$$

$$\overset{0}{Zn(s)} + \overset{+1+6-2}{H_2SO_4(aq)} \longrightarrow \overset{+2+6-2}{ZnSO_4(aq)} + \overset{0}{H_2(g)}$$

$$\overset{0}{Mg(s)} + \overset{+1-1}{2HCl(aq)} \longrightarrow \overset{+2\ -1}{MgCl_2(aq)} + \overset{0}{H_2(g)}$$

$$\overset{0}{2Al(s)} + \overset{+1-1}{6HCl(aq)} \longrightarrow \overset{+3-1}{2AlCl_3(aq)} + \overset{0}{3H_2(g)}$$

$$\overset{0}{Fe(s)} + \overset{+1-1}{2HCl(aq)} \longrightarrow \overset{+2-1}{FeCl_2(aq)} + \overset{0}{H_2(g)}$$

Metals like cadmium and tin which donot react with steam also react with acids to displace dihydrogen gas :

$$\overset{0}{Cd(s)} + \overset{+1-1}{2HCl(aq)} \longrightarrow \overset{+2\ -1}{CdCl_2(aq)} + \overset{0}{H_2(g)}$$

$$\overset{0}{Sn(s)} + \overset{+1\ -1}{2HCl(aq)} \longrightarrow \overset{+2\ -1}{SnCl_2(aq)} + \overset{0}{H_2(g)}$$

(*iv*) Very less reactive metals such as silver (Ag), gold (Au), etc which occur in the native state donot react even with dilute hydrochloric acid.

The above reactions may be used to prepare dihydrogen gas in the laboratory. The reactivity of the metals can be predicted from the rate of evolution of H_2 from water or aqueous acids . For example, sodium reacts with water very readily (fastest rate), magnesium reacts slowly while iron reacts at the slowest rate while silver and gold donot react at all.

We have already learnt that metals such as zinc (Zn), copper (Cu) and silver (Ag) though have the tendency to lose electrons, but their reducing tendency is in the order Zn > Cu > Ag.

Reactivity of non-metals. Like metals, there is also an activity series for non-metals, therefore, their reactivity depends upon their oxidising power. For

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example, oxidising power of halogens decreases as we move down the group 17 from fluorine to iodine. Thus, fluorine is the strongest oxidising agent. It can displace in their aqueous solutions Cl_2 from Cl^- ions, Br_2 from Br^- ions and I_2 from I^- ions. Thus, fluorine can show displacement reactions as :

$$2X^-(aq) + F_2(aq) \longrightarrow X_2(g) + 2F^-(aq)$$

where $X^- = Cl^-$, Br^- and I^-

In fact, fluorine is so reactive that it even attacks water and displaces the oxygen of water.

$$2H_2O(l) + 2F_2(g) \longrightarrow 4HF(aq) + O_2(g)$$

It is because of this reason, the displacement reactions of chlorine bromine or iodine using fluorine are usually not carried out in aqueous solutions.

On the other hand, chlorine can displace bromide and iodide ions in aqueous solution as shown below :

$$\overset{0}{Cl_2} + \overset{+1\ -1}{2KBr}(aq) \longrightarrow \overset{+1\ -1}{2KCl}(aq) + \overset{0}{Br_2}(l)$$

$$\overset{0}{Cl_2} + \overset{+1\ -1}{2KI}(aq) \longrightarrow \overset{+1\ -1}{2KCl}(aq) + I_2(s)$$

Since bromine and iodine are coloured and dissolve in CCl_4 or CS_2, these can be easily identified from the colour of their solution. The above reactions may be written in ionic from as :

$$2X^-(aq) + Cl_2(g) \longrightarrow X_2 + 2Cl^-(aq)\ (X^- = Br^-, I^-)$$

e.g.,
$$\overset{-1}{2Br^-}(aq) + \overset{0}{Cl_2}(g) \longrightarrow \overset{0}{Br_2}(l) + \overset{-1}{2Cl^-}(aq)$$

$$\overset{-1}{2I^-}(aq) + \overset{0}{Cl_2}(g) \longrightarrow \overset{0}{I_2}(s) + \overset{-1}{2Cl^-}(aq)$$

The above two reactions form the basis of identifying bromide (Br^-) and iodide (I^-) ions in the laboratory by carbon tetrachloride (CCl_4) or carbon disulphide (CS_2). This test is popularly known as **'layer test'**.

Similarly, bromine can displace iodine from iodide ion in the aqueous solution :

$$\overset{0}{Br_2}(l) + \overset{-1}{2I^-}(aq) \longrightarrow \overset{-1}{2Br^-}(aq) + \overset{0}{I_2}(s)$$

The above halogen displacement reactions have been widely used in the laboratory and industry. The halogens can be recovered from the corresponding halides by using suitable oxidising agents according to the reaction :

$$2X^-(aq) \xrightarrow{\text{Oxidising agent}} X_2 + 2e^-$$

(where X = halogen element)

It may be noted that although a number of oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$, $MnCl_2$, etc are available to oxidise Cl^-, Br^-, and I^- ions to liberate Cl_2, Br_2 and I_2 respectively, no oxidising agent is available to oxidise F^- ions to F_2. This is because, fluorine itself is the strongest oxidising agent. Therefore, the only method to prepare fluorine is to oxidise F^- ions electrolytically.

4. Disproportionation reactions

These are *the reactions in which an element in one oxidation state is simultaneously oxidised and reduced. In other words, one reacting substance in a disproportionation reaction always contains an element that can exhibit at least three oxidation states.* The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states exist for that element. The most common example is the decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

In this reaction, oxidation number of O decreases from – 1 to – 2 (in H_2O) and increases from – 1 to 0 (in O_2).

This may be simply represented as

Reduced

$$\overset{+1\ -1}{H_2O_2}(aq) \longrightarrow \overset{+1\ -2}{H_2O}(l) + \overset{0}{O_2}(g)$$

Oxidised

Some other examples are :

(*i*) Phosphorus and sulphur undergo disproportionation in alkaline medium as shown below:

$$P_4(s) + 3OH^-(aq) + 3H_2O\ (l) \longrightarrow PH_3\ (g) + 3H_2PO_2^-(aq)$$

In this reaction, oxidation number of P increases from 0 to + 1 (in $H_2PO_2^-$) and decreases from 0 to – 3 (in PH_3).

Reduced

$$\overset{0}{P_4}\ (s) + 3OH^-\ (aq) \longrightarrow \overset{-3}{PH_3}(g) + 3\overset{+1}{H_2PO_2^-}(aq)$$

Oxidised

(*ii*) $S_8(s) + 12OH^-(aq) \longrightarrow 4S^{2-}(aq) + 2S_2O_3^{2-}(aq) + 6H_2O$

In this reaction, oxidation number of S increases from 0 to + 2 (in $S_2O_3^{2-}$ ion) and decreases from 0 to – 2 (in S^{2-} ion).

Reduced

$$\overset{0}{S_8}(s) + 12OH^-(aq) \longrightarrow \overset{-2}{4S^{2-}}(aq) + \overset{+2}{2S_2O_3^{2-}}(aq) + 6H_2O$$

Oxidised

(*iii*) Chlorine also undergoes disproportionation in alkaline medium as :

Reduction

$$\overset{0}{Cl_2}(g) + 2OH^-(aq) \longrightarrow \overset{+1}{ClO^-}(aq) + \overset{-1}{Cl^-}(aq) + H_2O(l)$$

Oxidation

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This reaction forms the basis of preparing household bleaching agents. The hypochlorite (ClO^-) ion acts as a bleaching agent by oxidising the colouring matter (or stains) to colourless compounds.

Like chlorine, bromine and iodine also undergo similar disproportionation reactions. However, fluorine does not show this behaviour. This is because fluorine is the most electronegative and strongest oxidising agent and therefore, it does not show positive oxidation states. Therefore, fluorine reacts in different way forming oxygen difluoride as :

$$2\overset{0}{F_2}(g) + 2OH^-(aq) \longrightarrow 2\overset{-1}{F^-}(aq) + \overset{+2-1}{OF_2}(g) + H_2O(l)$$

It may be noted that F_2 also reacts with water to produce some oxygen.

There is another important disproportionation reaction. Copper (I) disproportionates to copper (II) and copper as :

$$2\,Cu^+ \longrightarrow Cu + Cu^{2+}$$

Reduction

$$\overset{+1}{2Cu^+} \longrightarrow \overset{0}{Cu} + \overset{+2}{Cu^{2+}}$$

Oxidation

Therefore, Cu(I) is unstable and only found in the solid state.

SOLVED EXAMPLES

Example 16.

Which of the two ClO_2^- or ClO_4^- show disproportionation reaction and why ?

Write reaction for the species that disproportionates.

Solution: The oxidation state of Cl in ClO_2^- is + 3 and in ClO_4^-, it is + 7. So, chlorine is present in highest oxidation state of + 7 in ClO_4^- and it cannot increase its oxidation state. Hence ClO_4^- does not disproportionates.

The disproportionation reaction of ClO_2^- is

$$\overset{+3}{3ClO_2^-} \longrightarrow \overset{-1}{Cl^-} + \overset{+5}{2ClO_3^-}$$

Example 17.

Write the disproportionation reactions of the following species :

(i) ClO^- (ii) ClO_3^- (iii) Cl^- (iv) ClO_2^- (v) ClO_4^- (vi) Tl^+

Solution:

(*i*) $\overset{+1}{3ClO^-} \longrightarrow \overset{-1}{2Cl^-} + \overset{+5}{ClO_3^-}$

(*ii*) $\overset{+5}{4ClO_3^-} \longrightarrow \overset{-1}{Cl^-} + \overset{+7}{3ClO_4^-}$

(*iii*) Cl^- does not disproportionates.

(*iv*) $\overset{+3}{3ClO_2^-} \longrightarrow \overset{-1}{Cl^-} + \overset{+5}{2ClO_3^-}$

(*v*) ClO_4^- does not disproportionate because in this oxoanion, chlorine is present in its highest oxidation state *i.e.*, + 7.

(*vi*) $3Tl^+ \rightleftharpoons \overset{0}{2Tl} + Tl^{3+}$

Example 18.

Classify the following redox reactions giving reasons: **N.C.E.R.T.**

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

(b) $2Pb(NO_3)(s) \longrightarrow 2PbO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

(c) $NaH(s) + H_2O(l) \longrightarrow NaOH\,(aq) + H_2(g)$

(d) $2NO_2(g) + 2OH^-(aq) \longrightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$

Solution:

(*a*) $\overset{0}{N_2}(g) + \overset{0}{O_2}(g) \longrightarrow \overset{+2\ -2}{2NO}(g)$

The compound nitric oxide is formed by the combination of elemental substances (N_2 and O_2). Therefore, it is a **combination redox reaction.**

(*b*) $\overset{+2\ +5\ -2}{2Pb(NO_3)_2}(s) \xrightarrow{Heat} \overset{+2\ -2}{2PbO}(s) + \overset{+4\ -2}{2NO_2}(g) + \frac{1}{2}\overset{0}{O_2}(g)$

Lead nitrate decomposes to form three products and therefore, it is a **decomposition redox reaction.**

(*c*) $\overset{+1\ -1}{NaH}(s) + \overset{+1\ -2}{H_2O}(l) \longrightarrow \overset{+1\ -2\ +1}{NaOH}\,(aq) + \overset{0}{H_2}(g)$

Hydrogen of water has been displaced by hydride ion to form dihydrogen gas. Therefore, it is **displacement redox** reaction.

(*d*) $\overset{+4}{2NO_2}(g) + 2OH^-(aq) \longrightarrow \overset{+3}{NO_2^-}(aq) + \overset{+5}{NO_3^-}(aq) + H_2O(l)$

In this reaction, the +4 oxidation state of nitrogen (in NO_2) decreases to +3 (in NO_2^-) and increases to +5 (in NO_3^-). Therefore, it is **disproportionation redox reaction.**

KEY NOTE

Pb_3O_4 reacts with HCl and HNO_3 quite differently as:

$$Pb_3O_4 + 8\,HCl \longrightarrow 3PbCl_2 + Cl_2 + 4H_2O$$

$$Pb_3O_4 + 4\,HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

Why does it react differently ? This is an interesting observation.

Pb_3O_4 is not a simple compound. It is a mixture of 2 mol of PbO and 1 mol of PbO_2 as 2 PbO. PbO_2.

In PbO_2, lead is present in + 4 oxidation state, whereas the stable oxidation state of lead in PbO is + 2. Therefore PbO_2 can act as an oxidising agent and can oxidise Cl^- ion in HCl to chlorine.

It may be noted that PbO is a basic oxide. Thus the reaction :

$$Pb_3O_4 + 8\,HCl \longrightarrow 3PbCl_2 + Cl_2 + 4H_2O$$

can be splitted into the following two reactions:

$2PbO + 4HCl \longrightarrow 2PbCl_2 + 2H_2O$: acid-base reaction

$\overset{+4}{PbO_2} + 4\overset{-1}{HCl} \longrightarrow \overset{+2}{PbCl_2} + \overset{0}{Cl_2} + H_2O$: redox reaction

However, nitric acid is itself an oxidising agent and therefore, no reaction occurs betwen PbO_2 and HNO_3. But the acid-base reaction between PbO and HNO_3 may occur as :

$$2PbO + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O$$

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The complete reaction may be written as :

$Pb_3O_4 + 4\ HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

Thus, it is the passive nature of PbO_2 against HNO_3 which results in different reactions of Pb_3O_4 with HNO_3 than those with HCl.

BALANCING OXIDATION–REDUCTION REACTIONS

Though there are a number of methods for balancing oxidation-reduction reactions, two methods are very important. These are :

1. Oxidation number method

2. Ion-electron method or half equation method.

1. Oxidation number method.

We have learnt that during oxidation, there is always increase in oxidation number and during reduction there is always decrease in oxidation number. Therefore, during a redox reaction, the *total increase in oxidation number must be equal to total decrease in oxidation number.* This is the basic principle for balancing the chemical equations. In addition, the law of conservation of mass should not be violated, *i.e.*, the number of atoms of each kind on one side of the equation must be equal to the number of atoms of the corresponding elements on the other side. The following steps should be followed :

Steps for Balancing Redox Equations by Oxidation Number Method

Step 1. Write the skeletal redox equation for all the known reactants and products of the reaction.

Step 2. Indicate the oxidation number of all the atoms in each compound above the symbol of the element.

Step 3. Identify the element or elements which undergo a change in oxidation number. Usually only two elements will be involved, one whose oxidation number increases (*i.e.* reducing agent) and the other whose oxidation number decreases (*i.e.* oxidising agent).

Step 4. Calculate the increase or decrease in oxidation numbers per atom. If more than one atom of the same element is involved, find out the total increase or decrease in O.N. Then multiply this number of increase/decrease of O. N. with the number of atoms which are undergoing the change.

Step 5. Equate the increase in oxidation number with decrease in oxidation number on the reactant side by multiplying the formulae of the oxidising and reducing agents.

Step 6. Balance the equation with respect to all other atoms except hydrogen and oxygen.

Step 7. Finally, balance hydrogen and oxygen. For balancing for oxygen atoms add water molecules to the side deficient in it. Balancing of hydrogen atoms depend upon the medium (acidic or basic) as explained below :

(i) For reactions taking place in **acidic solutions,** add H^+ ions to the side deficient in hydrogen atoms.

(ii) For reactions taking place in **basic solutions,** add H_2O molecules to the side deficient in hydrogen atoms and simultaneously add equal number of OH^- ions on the other side of the equation.

Step 8. Finally balance the equation by cancelling common species present on both sides of the equation.

Let us discuss the above method stepwise with the help of reaction between zinc and hydrochloric acid.

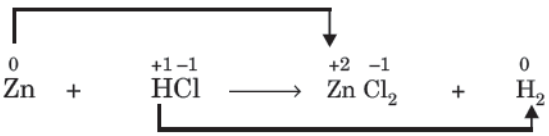
Step 1. The skeleton equation is :

$$Zn + HCl \longrightarrow ZnCl_2 + H_2$$

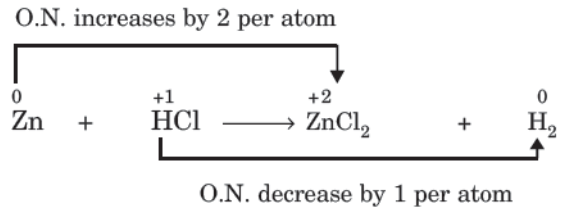
Step 2. Oxidation number of various atoms involved in the reaction :

$$\overset{0}{Zn} + \overset{+1\ -1}{HCl} \longrightarrow \overset{+2\ -1}{ZnCl_2} + \overset{0}{H_2}$$

Step 3. The oxidation number of zinc has increased from 0 to +2 while that of hydrogen has decreased from +1 to 0. However, the oxidation number of chlorine remains the same on both sides of the equation. Therefore, zinc is reducing agent while HCl is oxidising agent in this reaction and the changes are shown as :



Step 4. The increase and decrease in oxidation number per atom can be indicated as :



Step 5. The increase in oxidation number of 2 per atom can be balanced with decrease in oxidation number of 1 per atom if Zn atoms are multiplied by 1 and HCl by 2. Consequently the equation will be :

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Step 6. Balance all other atoms on both sides of the equation. By chance, they are equal, otherwise equate them.

Hence, **balanced chemical equation** is :

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

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Example 19.

Copper reacts with nitric acid. A brown gas is formed and the solution turns blue. The equation may be written as :

$$Cu + NO_3^- \longrightarrow NO_2 + Cu^{2+}$$

Balance the equation by oxidation number method.

Solution: Step 1. Skeleton equation

$$Cu + NO_3^- \longrightarrow NO_2 + Cu^{2+}$$

Step 2. Writing oxidation numbers of each atom

$$\overset{0}{Cu} + \overset{+5\,-2}{NO_3^-} \longrightarrow \overset{+4\,-2}{NO_2} + \overset{+2}{Cu^{2+}}$$

Step 3.

$$\overset{0}{Cu} + \overset{+5}{NO_3^-} \longrightarrow \overset{+4}{NO_2} + \overset{+2}{Cu^{2+}}$$

The oxidation number of copper has increased from 0 to +2 while that of nitrogen has decreased from +5 to +4.

Step 4. Show the increase/decrease of oxidation number

O.N. increases by 2 per atom

$$\overset{0}{Cu} + \overset{+5}{NO_3^-} \longrightarrow \overset{+4}{NO_2} + \overset{+2}{Cu^{2+}}$$

O.N. decreases by 1 per atom

Step 5. Balance the increase/decrease in oxidation number by multiplying NO_3^- by 2 and Cu by 1.

$$Cu + 2NO_3^- \longrightarrow NO_2 + Cu^{2+}$$

Step 6. Balance other atoms except H and O as

$$Cu + 2NO_3^- \longrightarrow 2NO_2 + Cu^{2+}$$

Step 7. Reaction takes place in acidic medium, so add H^+ ions to the side deficient in H^+ and balance H and O atoms :

$$Cu + 2NO_3^- + 4H^+ \longrightarrow 2NO_2 + Cu^{2+} + 2H_2O$$

Example 20.

Balance the following equations :

(i) $Fe_2O_3 + C \longrightarrow Fe + CO$

(ii) $Fe^{2+} + Cr_2O_7^{2-} + H^+ \longrightarrow Fe^{3+} + Cr^{3+} + H_2O$

(iii) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO_2 + H_2O$

(iv) $C_6H_6 + O_2 \longrightarrow CO_2 + H_2O$

Solution: *(i)* $Fe_2O_3 + C \longrightarrow Fe + CO$

1. The skeleton equation along with oxidation number of each atom is :

$$\overset{+3\ -2}{Fe_2O_3} + \overset{0}{C} \longrightarrow \overset{0}{Fe} + \overset{+2\ \ -2}{CO}$$

2. The oxidation number of C increases from 0 to +2 while that of Fe decreases from +3 to 0. Therefore, the equation may be written as

O.N. increases by 2 per atom

$$\overset{+3}{Fe_2O_3} + \overset{0}{C} \longrightarrow \overset{0}{Fe} + \overset{+2}{CO}$$

O.N. decreases by 3 per atom

3×2 per 2 atoms

3. To balance increase or decrease multiply C by 3 and Fe_2O_3 by 1 as :

$$Fe_2O_3 + 3\,C \longrightarrow Fe + CO$$

4. Balancing all other atoms, we get

$$Fe_2O_3 + 3C \longrightarrow 2\,Fe + 3\,CO$$

(ii) $Fe^{2+} + Cr_2O_7^{2-} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

1. The skeleton equation along with oxidation number of each atom

$$\overset{+2}{Fe^{2+}} + \overset{+6\ -2}{[Cr_2O_7]^{2-}} + \overset{+1}{H^+} \longrightarrow \overset{+3}{Fe^{3+}} + \overset{+3}{Cr^{3+}} + \overset{+1\ -2}{H_2O}$$

2. The oxidation number of chromium decreases from +6 in $Cr_2O_7^{2-}$ to +3 in Cr^{3+}. The total decrease for two chromium atoms in $Cr_2O_7^{2-}$ to Cr^{3+} is 6. On the other hand, the oxidation number of iron increases from +2 (in Fe^{2+}) to +3 (in Fe^{3+}). Therefore, the equation can be written as :

O.N. increases by 1 per atom

$$\overset{+2}{Fe^{2+}} + \overset{+6}{[Cr_2O_7]^{2-}} + H^+ \longrightarrow \overset{+3}{Fe^{3+}} + \overset{+3}{Cr^{3+}} + \overset{+1}{H_2O}$$

O.N. decreases by 6 for 2 Cr atoms

3. To balance increase and decrease of oxidation numbers, multiply Fe^{2+} by 6 and $Cr_2O_7^{2-}$ by 1. Then we get

$$6Fe^{2+} + Cr_2O_7^{2-} + H^+ \longrightarrow Fe^{3+} + Cr^{3+} + H_2O$$

4. On counting and equating the atoms on both sides, we get the balanced equation as :

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(iii) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO_2 + H_2O$

1. The skeleton equation along with oxidation number of various atoms is

$$\overset{0}{Zn} + \overset{+1+5-2}{HNO_3} \longrightarrow \overset{+2\ +5-2}{Zn(NO_3)_2} + \overset{+4\ -2}{NO_2} + \overset{+1\ -2}{H_2O}$$

O.N. increases by 2

2.

$$\overset{0}{Zn} + \overset{+5}{HNO_3} \longrightarrow \overset{+2}{Zn(NO_3)_2} + \overset{+4}{NO_2} + H_2O$$

O.N. decreases by 1

3. Multiply HNO_3 by 2

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + NO_2 + H_2O$$

It has been observed that part of nitrogen undergoes no change in oxidation number in forming $Zn(NO_3)_2$. However, in order to balance additional two NO_3^- ions, add $2HNO_3$ more on the left hand side as :

$$Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + NO_2 + H_2O$$

4. Balance all other atoms.

$$Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

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(*iv*) $C_6H_6 + O_2 \longrightarrow CO_2 + H_2O$

1. The skeleton equation along with oxidation number of each atom :

$\overset{-1\ +1}{C_6H_6} + \overset{0}{O_2} \longrightarrow \overset{+4\ -2}{CO_2} + \overset{+1\ -2}{H_2O}$

O.N. increases by 5 per atom

or 5 × 6 per 6 atoms

2. $\overset{-1}{C_6H_6} + \overset{0}{O_2} \longrightarrow \overset{+4}{CO_2} + \overset{-2}{H_2O}$

O.N. decreases by 2 per atom or 2 × 2 per molecule

3. Multiply C_6H_6 by 2 and O_2 by 15 to balance increase and decrease in O.N.

$2C_6H_6 + 15O_2 \longrightarrow CO_2 + H_2O$

4. Balance all atoms

$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$

❑ Example 21.

Permangnate ion reacts with bromide ion in basic medium to give managanese dioxide and bromate ion. Write the balanced chemical equation for the reaction. ***N.C.E.R.T.***

Solution: The chemical equation is :

$MnO_4^- + Br^- \longrightarrow MnO_2 + BrO_3^-$

1. The skeleton equation with oxidation number of each atom is :

$\overset{+7\ -2}{MnO_4^-} + \overset{-1}{Br^-} \longrightarrow \overset{+4\ -2}{MnO_2} + \overset{+5\ -2}{BrO_3^-}$

O.N. decreases by 3 per atom

$\overset{+7}{MnO_4^-} + \overset{-1}{Br^-} \longrightarrow \overset{+4}{MnO_2} + \overset{+5}{BrO_3^-}$

O.N. increases by 6 per atom

2. To balance increase and decrease in oxidation numbers, multiply MnO_4^- by 2.

$2MnO_4^- + Br^- \longrightarrow MnO_2 + BrO_3^-$

3. Balance all atoms other than H and O.

$2MnO_4^- + Br^- \longrightarrow 2MnO_2 + BrO_3^-$

4. Since the reaction occurs in basic medium, add OH^- ions to right hand side.

$2MnO_4^- + Br^- \longrightarrow 2MnO_2 + BrO_3^- + OH^-$

5. To add H atoms, add H_2O molecules on the left hand side and equal number of OH^- ions on the right hand side

$2MnO_4^- + Br^- + H_2O \longrightarrow 2MnO_2 + BrO_3^- + OH^- + OH^-$

or $2MnO_4^- + Br^- + H_2O \longrightarrow 2MnO_2 + BrO_3^- + 2OH^-$

❑ Example 22.

Balance the following reactions by oxidation number method :

(*i*) $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$

(*ii*) $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$ *(in acidic medium)*

(*iii*) $Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$ *(in basic medium)*

Solution: (*i*) $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$

1. The skeleton equation with oxidation number is :

$\overset{+2\ -1}{FeS_2} + \overset{0}{O_2} \longrightarrow \overset{+3\ -2}{Fe_2O_3} + \overset{+4\ -2}{SO_2}$

(**Note :** Oxidation number of S in FeS_2 is –1 and not –2).

2. The oxidation number of iron as well as sulphur increases from +2 to +3 and –1 to +4 respectively. Since Fe and S must maintain their atomic ratio, the change in oxidation number will be considered together. On the other hand, the oxidation number of oxygen decreases from 0 to –2. Thus,

O.N. increases 1 per Fe and 5 per S atom

i.e. 1 + 2 × 5 = 11 per FeS_2

$\overset{+2\ -1}{FeS_2} + \overset{0}{O_2} \longrightarrow \overset{+3}{Fe_2O_3} + \overset{+4\ -2}{SO_2}$

O.N. decreases by 2 per atom or 4 per O_2

3. To balance increase and decrease of oxidation number, multiply FeS_2 by 4 and O_2 by 11.

$4FeS_2 + 11O_2 \longrightarrow Fe_2O_3 + SO_2$

4. Balancing all atoms

$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

(*ii*) $MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

1. The skeleton equation along with oxidation number of each atom is as :

$\overset{+7\ -2}{Mn\ O_4^-} + \overset{+2}{Fe^{2+}} + H^+ \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+3}{Fe^{3+}} + \overset{+1\ -2}{H_2O}$

O.N. decreases by 5 per atom

$\overset{+7}{MnO_4^-} + \overset{+2}{Fe^{2+}} + H^+ \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+3}{Fe^{3+}} + H_2O$

O.N. increases by 1 per atom

2. The oxidation number of Mn decreases from +7 to +2 while that of Fe increases from +2 to +3.

3. Multiply Fe^{2+} by 5 and MnO_4^- by 1 to balance increase and decrease in oxidation number.

$MnO_4^- + 5Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

4. Balance all atoms (except H and O)

$MnO_4^- + 5Fe^{2+} + H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + H_2O$

This reaction takes place in **acidic medium.** The O and H atoms are balanced as given below :

5. Balance O-atoms by adding equal number of H_2O molecules as :

$MnO_4^- + 5Fe^{2+} + H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + H_2O + 3H_2O$

6. Balance H-atoms by adding H^+ ions on the side deficient in H-atoms.

$MnO_4^- + 5Fe^{2+} + H^+ + 7H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

or $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

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Let us **sum up** the methods for balancing O and H-atoms in oxidation-reduction reaction taking placing in **acidic medium.**

1. **Balance O-atoms by adding H_2O molecules on the side deficient in O-atoms.**
2. **To balance H-atoms, add H^+ ions (available in acid solution) on the side deficient in H-atoms.**

(iii) $Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$ (in alkaline medium)

1. The skeleton equation along with oxidation number of each atom is :

$$\overset{+3\ -2\ +1}{Cr(OH)_3} + \overset{+5-2}{IO_3^-} \longrightarrow \overset{-1}{I^-} + \overset{+6\ -2}{CrO_4^{2-}}$$

O.N. increases by 3 per atom

$$\overset{+3}{Cr(OH)_3} + \overset{+5}{IO_3^-} \longrightarrow \overset{-1}{I^-} + \overset{+6}{CrO_4^{2-}}$$

O.N. decreases by 6 per atom

2. To balance increase or decrease in oxidation numbers, multiply $Cr(OH)_3$ by 2 and IO_3^- by one.

$2Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$

3. Balance all atoms (other than H and O).

$2Cr(OH)_3 + IO_3^- \longrightarrow I^- + 2CrO_4^{2-}$

4. Reaction takes place in basic medium, add OH^- to right hand side to balance O-atoms.

$2Cr(OH)_3 + IO_3^- \longrightarrow I^- + 2CrO_4^{2-} + OH^-$

5. To balance H-atoms, add H_2O molecules on right hand side and equal number of OH^- on left hand side.

$2Cr(OH)_3 + IO_3^- + 5OH^- \rightarrow I^- + 2CrO_4^{2-} + OH^- + 5H_2O$

or $2Cr(OH)_3 + IO_3^- + 4OH^- \rightarrow I^- + 2CrO_4^{2-} + 5H_2O$

Let us **sum up** the method for balancing O and H atoms in oxidation-reduction reactions taking place in **basic medium.**

1. **Balance O atoms by adding OH^- ions (available from basic solution) on the side deficient in O-atoms (step 5)**
2. **To balance H atoms, add one molecule of water for each H-atom needed on the side deficient in H atom. At the same time add an equal number of OH^- ions to the opposite side.**

❑ Example 23.

Balance the following equations by oxidation number method :

(i) $As_2S_3(s) + NO_3^-(aq) \longrightarrow AsO_4^{3-}(aq) + NO(g) + S(s)$ *(acidic medium)*

(ii) $MnO_4^-(aq) + C_2H_2O_4(aq) \longrightarrow Mn^{2+}(aq) + CO_2(g) + H_2O(l)$ *(acidic medium)*

(iii) $P + HNO_3 \longrightarrow H_3PO_4 + H_2O + NO_2$

Solution: *(i)* $As_2S_3 + NO_3^- \longrightarrow AsO_4^{3-} + NO + S$

1. The skeleton equation with oxidation number of each atom is :

$$\overset{+3\ -2}{As_2S_3} + \overset{+5\ -2}{NO_3^-} \longrightarrow \overset{+5\ -2}{AsO_4^{3-}} + \overset{+2-2}{NO} + \overset{0}{S}$$

2. The O.N. of As increases from +3 to +5 and that of S increases from –2 to 0. The O.N. of N decreases from +5 to +2. This means that both As and S have been oxidised while NO_3^- has been reduced. Since As and S must maintain their atomic ratio of 2:3 (as in As_2S_3), therefore, the change in O.N. of these two atoms must be considered together. Thus,

O.N. increases by 2 per As and 2 per S atom ie $2 \times 2 + 2 \times 3 = 10$ per As_2S_3

$$\overset{+3\ -2}{As_2S_3} + \overset{+5}{N\,O_3^-} \longrightarrow \overset{+5\ 3-}{AsO_4^{3-}} + \overset{+2}{NO} + \overset{0}{S}$$

O.N. decreases by 3 per atom

3. To balance increase and decrease of O.N., multiply As_2S_3 by 3 and NO_3^- by 10.

$3As_2S_3 + 10NO_3^- \longrightarrow AsO_4^{3-} + NO + S$

4. Balance all atoms (except H and O)

$3As_2S_3 + 10NO_3^- \longrightarrow 6AsO_4^{3-} + 10NO + 9S$

This reaction takes place in acidic medium. The O and H atoms are balanced as :

5. Balance O atoms by adding equal number of H_2O molecules as :

$3As_2S_3 + 10NO_3^- + 4H_2O \longrightarrow 6AsO_4^{3-} + 10NO + 9S$

6. Balance H atoms by adding H^+ ions on the side deficient in H atoms :

$3As_2S_3 + 10NO_3^- + 4H_2O \longrightarrow 6AsO_4^{3-} + 10NO + 9S + 8H^+.$

(ii) $MnO_4^- + C_2H_4O_4 \longrightarrow Mn^{2+} + CO_2 + H_2O$

1. The skeleton equation with O.N. of each atom is :

$$\overset{+7\ -2}{MnO_4^-} + \overset{+3\ +1\ -2}{C_2H_2O_4} \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+4\ -2}{CO_2} + \overset{+1\ -2}{H_2O}$$

2. The O.N. of C increases from +3 to +4 and the O.N. of Mn decreases from +7 to +2. Thus,

O.N. increases by 1 per atom or 2 per molecule

$$\overset{+7}{MnO_4^-} + \overset{+3}{C_2H_2O_4} \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+4}{CO_2} + H_2O$$

O.N. decreases by 5 per atom

3. To balance increase and decrease in O.N. multiply MnO_4^- by 2 and $C_2H_2O_4$ by 5.

$2MnO_4^- + 5C_2H_2O_4 \longrightarrow 2Mn^{2+} + CO_2 + H_2O$

4. Balance all atoms (except H and O)

$2MnO_4^- + 5C_2H_2O_4 \longrightarrow 2Mn^{2+} + 10CO_2 + H_2O$

This reaction takes place in acidic medium. The O and H atoms are balanced as :

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5. Balance O atoms by adding equal number of H_2O molecules as :

$$2MnO_4^- + 5C_2H_2O_4 \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

6. To balance H atoms add H^+ ions on the side deficient in H atoms :

$$2MnO_4^- + 5C_2H_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(*iii*) $P + HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$

1. The skeleton equation with O.N. of each atom is :

$$\overset{0}{P} + \overset{+1\,+5\,-2}{HNO_3} \longrightarrow \overset{+1\,+5\,-2}{H_3PO_4} + \overset{+4\,-2}{NO_2} + \overset{+1\,-2}{H_2O}$$

2. The O.N. of P increases from 0 to +5 and the O.N. of N decreases from +5 to +4. Thus,

O.N. increases by 5 per atom

$$\overset{0}{P} + \overset{+5}{HNO_3} \longrightarrow \overset{+5}{H_3PO_4} + \overset{+4}{NO_2} + H_2O$$

O.N. decreases by 1 per atom

3. To balance increase and decrease in O.N. multiply HNO_3 by 5.

$$P + 5HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$$

4. Balance all atoms (except H and O)

$$P + 5HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$$

This is balanced equation.

❑ Example 24.

Write the balanced ionic equation for the reaction of potassium dichromate (VI), $K_2Cr_2O_7$ with sodium sulphite, Na_2SO_3 in acid medium to give chromium(III) ion and sulphate ion. ***N.C.E.R.T.***

Solution : The skeleton equation is :

$$Cr_2O_7^{2-} + SO_3^{2-} \longrightarrow Cr^{3+} + SO_4^{2-}$$

1. The skeleton equation with oxidation number is :

$$\overset{+6\,-2}{Cr_2O_7^{2-}} + \overset{+4\,-2}{SO_3^{2-}} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{+6\,-2}{SO_4^{2-}}$$

2. O.N. increases by 2 per atom

$$\overset{+6}{Cr_2O_7^{2-}} + \overset{+4}{SO_3^{2-}} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{+6}{SO_4^{2-}}$$

O.N. decreases by 3 × 2 per molecule

3. To balance increase and decrease multiply SO_3^{2-} by 3

$$Cr_2O_7^{2-} + 3SO_3^{2-} \longrightarrow Cr^{3+} + SO_4^{2-}$$

4. Balance all atoms (except O and H)

$$Cr_2O_7^{2-} + 3SO_3^{2-} \longrightarrow 2Cr^{3+} + 3SO_4^{2-}$$

This reaction occurs in acidic medium, O and H atoms are balanced as :

5. Balance O atoms by adding H_2O molecules as :

$$Cr_2O_7^{2-} + 3SO_3^{2-} \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

6. Balance H atoms by adding H^+ ions on the side deficient in H atoms :

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

This is a **balanced equation**.

Practice Problems

◑ **10.** Balance the following equations by oxidation number method :

(*a*) $MnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

(*b*) $H_2S + KMnO_4 + H_2SO_4 \longrightarrow KHSO_4 + MnSO_4 + S + H_2O$

(*c*) $CuO + NH_3 \longrightarrow Cu + N_2 + H_2O$

◑ **11.** Balance the following ionic equations by oxidation number method :

(*i*) $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + H_2O$ (acidic medium)

(*ii*) $Zn + NO_3 \longrightarrow Zn^{2+} + NH_4^+$ (basic medium)

(*iii*) $H_2S + MnO_4^- \longrightarrow S + Mn^{2+} + H_2O$ (acidic medium)

(*iv*) $Cu + NO_3^- + H^+ \longrightarrow NO_2 + Cu^{2+}$

(*v*) $MnO_4^- + H_2C_2O_4 \longrightarrow Mn^{2+} + CO_2 + H_2O$ (acidic medium)

◑ **12.** Magnesium reacts with nitric acid to give magnesium nitrate in aqueous solution, nitrous oxide gas and liquid water. Write balanced equation for this redox reaction.

◑ **13.** Balance the following equations by oxidation number method :

(*i*) $H_2S\,(aq) + Cl_2\,(g) \longrightarrow S\,(s) + Cl^-\,(aq)$ (acidic medium)

(*ii*) $Cl_2O_7\,(g) + H_2O_2\,(g) \longrightarrow ClO_2^-\,(aq) + O_2\,(g)$ (basic medium)

(*iii*) $P\,(s) + OH^-\,(aq) \longrightarrow PH_3\,(g) + H_2PO_2^-\,(aq)$ (basic medium)

(*iv*) $N_2H_4\,(g) + ClO_3^-\,(aq) \longrightarrow NO\,(g) + 4Cl^-\,(g)$

(*v*) $MnO_4^-(aq) + C_2H_2O_4 \longrightarrow Mn^{2+}(aq) + CO_2(g) + H_2O\,(l)$

(*vi*) $MnO_4^-(aq) + C_2H_5OH \longrightarrow Mn^{2+}(aq) + CH_3COOH\,(aq)$

Answers to Practice Problems

◐ **10.** (*a*) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

(*b*) $5H_2S + 2KMnO_4 + 4H_2SO_4 \longrightarrow 2KHSO_4 + 2MnSO_4 + 5S + 8H_2O$

(*c*) $3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$

◐ **11.** (*i*) $2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$

(*ii*) $4Zn + NO_3^- + 7H_2O \longrightarrow 4Zn^{2+} + NH_4^+ + 10\,OH^-$

(*iii*) $5H_2S + 2MnO_4^- + 6H^+ \longrightarrow 5S + 2Mn^{2+} + 8H_2O$

(*iv*) $Cu + 2NO_3^- + 4H^+ \longrightarrow 2NO_2 + Cu + 2H_2O$

(*v*) $2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10\,CO_2 + 8H_2O$

◐ **12.** $4Mg(s) + 10HNO_3\,(aq) \longrightarrow 4Mg(NO_3)_2\,(aq) + N_2O\,(g) + 5H_2O(l)$

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13.(*i*) $H_2S\,(aq) + Cl_2\,(g) \longrightarrow S\,(s) + 2Cl^-\,(aq) + 2H^+\,(aq)$

(*ii*) $Cl_2O_7\,(g) + 4H_2O_2\,(aq) + 2OH^-(aq) \longrightarrow 2ClO_2^-\,(aq) + 4O_2\,(g) + 5H_2O\,(l)$

(*iii*) $4P\,(s) + 3OH^-\,(aq) + 3H_2O\,(l) \longrightarrow PH_3\,(g) + 3H_2PO_2^-\,(aq)$

(*iv*) $3N_2H_4\,(s) + 4ClO_3^-\,(aq) \longrightarrow 6NO\,(g) + 4Cl^-\,(aq) + 6H_2O\,(l)$

(*v*) $2MnO_4^-(aq) + 6H^+(aq) + 5C_2H_2O_4(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O\,(l)$

(*vi*) $4MnO_4^-(aq) + 5C_2H_5OH(aq) + 12H^+(aq) \longrightarrow 4Mn^{2+}(aq) + 5CH_3COOH\,(aq) + 11H_2O$

B. Ion-Electron Method (Balancing Equations Using Half Reactions)

The balancing of chemical equation by ion-electron method (using half reactions) is done by the following steps :

Step 1. Find the elements whose oxidation numbers are changed. Choose the substance which acts as an oxidising agent and one that acts as a reducing agent.

Step 2. Separate the complete equation into two half reactions, one for the change undergone by the oxidising agent and the other for the change undergone by the reducing agent.

Step 3. Balance half equations by the following steps :

(*i*) balance all atoms other than H and O.

(*ii*) calculate the oxidation number on both sides of the equation. Add electrons to whichever side is necessary, to make up the difference.

(*iii*) balance the half equation so that both sides get the same charge.

(*iv*) add water molecules to complete the balancing of the equation.

Step 4. Add two balanced half equations. Multiply one or both half equations by suitable numbers so that on adding the two equations, the electrons are balanced.

It may be noted that redox reaction may take place in all the three media *i.e.*, acidic or basic or neutral. If H^+ ions appear on either side of the equation, the reaction takes place in acidic medium. If OH^- ions appear on either side of the equation, the solution is basic. If neither H^+ nor OH^- ions are present, the reaction occurs in neutral solution. For balancing redox reactions involving acidic and basic media, the method has to be modified slightly as illustrated in the examples given ahead :

SOLVED EXAMPLES

❑ Example 25.

Consider the reaction between iron (II) ions and dichromate ions in acidic solution as :

$Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

Solution:

Step 1. Separate the equation into two half reactions :

The oxidation number of various atoms are shown below :

$$\overset{+6\ -2}{Cr_2O_7^{2-}} + \overset{+2}{Fe^{2+}} + \overset{+1}{H^+} \rightarrow \overset{+3}{Cr^{3+}} + \overset{+3}{Fe^{3+}} + \overset{+1\ -2}{H_2O}$$

In this case, chromium undergoes reduction, oxidation number decreases from +6 (in $Cr_2O_7^{2-}$) to +3 (in Cr^{3+})

Fe^{2+} (O.N. = +2) changes to Fe^{3+} (O.N. = +3). The species undergoing oxidation and reduction are :

Oxidation : $Fe^{2+} \longrightarrow Fe^{3+}$

Reduction : $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Step 2. Balance each half reaction separately as :

(*a*) $Fe^{2+} \longrightarrow Fe^{3+}$

(*i*) Balance all atoms other than H and O. This step is not needed, because, it is already balanced.

(*ii*) The oxidation number on left is +2 and on right is +3. To account for the difference, the electron is added to the right as :

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

(*iii*) Charge is already balanced.

(*iv*) No need to add H or O.

The balanced half equation is :

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad ...(i)$$

Consider the second half equation

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

(*i*) Balance the atoms other than H and O.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

(*ii*) The oxidation number of chromium on the left is +6 and on the right is +3. Each chromium atom must gain three electrons. Since there are two Cr atoms, add $6e^-$ on the left.

$$Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+}$$

(*iii*) Since the reaction takes place in acidic medium add $14H^+$ on the left to equate the net charge on both sides.

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+}$$

(*iv*) To balance H atoms, add $7H_2O$ molecules on the right.

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O \quad ...(ii)$$

This is the balanced half equation.

Step 3. Now add up the two half equations. Multiply eq. (i) by 6 so that electrons are balanced.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

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The balanced equation is :

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Note. If we carefully see step 2 part (*iii*) and (*iv*) we get a method for balancing redox reaction in acidic medium. Charge is balanced by adding H^+ and then appropriate number of H_2O molecules are added on the other side.

❑ **Example 26.**

Balance the following equations by ion electron method :

(a) $Cr_2O_7^{2-} + C_2H_4O \longrightarrow C_2H_4O_2 + Cr^{3+}$ *(in acidic medium)*

(b) $Zn + NO_3^- \longrightarrow Zn^{2+} + NH_4^+$ *(in basic medium)*

Solution:

Step 1. Separate the equation into the half reactions :

$$Cr_2O_7^{2-} + C_2H_4O \longrightarrow C_2H_4O_2 + Cr^{3+}$$

Write the oxidation number of the various atoms.

$$\overset{+6}{[Cr_2O_7^{2-}]} + \overset{-1}{C_2H_4O} \longrightarrow \overset{0}{C_2H_4O_2} + \overset{+3}{Cr^{3+}}$$

The species undergoing change in oxidation number are :

Oxidation : $\overset{-1}{C_2H_4O} \longrightarrow \overset{0}{C_2H_4O_2}$

Reduction : $\overset{+6}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}}$

Step 2. Balance each half reaction separately as :

(*a*) $C_2H_4O \longrightarrow C_2H_4O_2$

(*i*) The equation is already balanced in terms of carbon atoms.

(*ii*) The O.N. of carbon on the left is –1 while on the right, it is 0. To account for the difference in oxidation number, add two electrons on the right.

$$C_2H_4O \longrightarrow C_2H_4O_2 + 2e^-$$

(*iii*) & (*iv*) Since the reaction is taking place in acidic medium, and $2H^+$ on the right and a H_2O molecule on the left

$$C_2H_4O + H_2O \longrightarrow C_2H_4O_2 + 2e^- + 2H^+$$

(*b*) Balancing of reduction half reaction :

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

(*i*) Balance the Cr atoms on both sides of the equation

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

(*ii*) The O.N. of Cr atom on the left is +6 and on the right is +3. Thus, each Cr atom has gained three electrons *i.e.* total number of electrons gained is six. Add six electrons on the reactant side to account for difference in O.N.

$$Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+}$$

(*iii*) & (*iv*). As the reaction is proceeding in acidic medium add $14H^+$ on the left to equate the net charge on both sides. At the same time, add $7H_2O$ to right.

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Step 3. Adding the two half reactions.

Now add up the two half reactions to get the final equation. But before doing so, multiply the oxidation half reaction by 3 to equate the number of electrons.

$$C_2H_4O + H_2O \longrightarrow C_2H_4O_2 + 2e^- + 2H^+] \times 3$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$3C_2H_4O + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3C_2H_4O_2 + 2Cr^{3+} + 4H_2O$$

(*b*) $Zn + NO_3^- \longrightarrow Zn^{2+} + NH_4^+$

Step 1. Write oxidation number of each atom and split the equation into two half equations :

$$\overset{0}{Zn} + \overset{+5}{N}\,\overset{-2}{O_3^-} \longrightarrow \overset{+2}{Zn^{2+}} + \overset{-3\,+1}{N\,H_4^+}$$

In this reaction, zinc undergoes oxidation and NO_3^- undergoes reduction :

Oxidation : $Zn \longrightarrow Zn^{2+}$

Reduction : $NO_3^- \longrightarrow NH_4^+$

Step 2. Balance each half reaction separately as :

(*a*) $Zn \longrightarrow Zn^{2+}$

(*i*) Balance all atoms other than H and O (already done)

(*ii*) Add electrons to make up the difference in oxidation number,

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad ...(i)$$

(*iii*) Balance the charges (already done)

(*iv*) No need to add water.

The balanced oxidation half reaction is :

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

(*b*) $NO_3^- \longrightarrow NH_4^+$

(*i*) Balance all atoms other than H and O (already done).

(*ii*) Nitrogen changes its oxidation number from +5 to –3 and there is difference of 8 electrons. To balance the electrons :

$$NO_3^- + 8e^- \longrightarrow NH_4^+$$

(*iii*) Balance the charges. Since the reaction takes place in basic medium, add 10 OH^- ions on the right side.

$$NO_3^- + 8e^- \longrightarrow NH_4^+ + 10\ OH^-$$

(*iv*) Add water molecules to complete balancing,

$$NO_3^- + 8e^- + 7H_2O \longrightarrow NH_4^+ + 10\ OH^- \quad ...(ii)$$

Step 3. To add up the two half reactions, multiply eq. (*i*) by 4 as :

$$Zn \longrightarrow Zn^{2+} + 2e^-] \times 4$$
$$NO_3^- + 7H_2O + 8e^- \longrightarrow NH_4^+ + 10\ OH^-$$

$$4Zn + NO_3^- + 7H_2O \longrightarrow 4Zn^{2+} + NH_4^+ + 10\ OH^-$$

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❑ **Example 27.**

Balance the following redox equations by half reaction method :

(a) $Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$ *(in basic medium)*

(b) $MnO_4^- + SO_3^- \longrightarrow Mn^{2+} + SO_4^{2-}$ *(in acidic medium)*

(c) $Br_2 + H_2O_2 \longrightarrow BrO_3^- + H_2O$ *(in acidic medium)*

Solution: (*a*) $Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$

Step 1. Separate the equation into two half reactions :

$Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$

Write the oxidation number of various atoms.

$\overset{+3}{Cr}(OH)_3 + \overset{+5}{IO_3^-} \longrightarrow \overset{-1}{I^-} + \overset{+6}{CrO_4^{2-}}$

The species undergoing change in oxidation number are :

Oxidation : $\overset{+3}{Cr}(OH)_3 \longrightarrow \overset{+6}{CrO_4^{2-}}$

Reduction : $\overset{+5}{IO_3^-} \longrightarrow \overset{-1}{I^-}$

Step 2. Balance each half reaction separately as :

(*i*) $Cr(OH)_3 \longrightarrow CrO_4^{2-}$

The O.N. of Cr on the left is +3 and on the right it is +6. To account for the difference add 3 electrons on the right.

$Cr(OH)_3 \longrightarrow CrO_4^{2-} + 3e^-$

Since, it is occurring in basic medium

$Cr(OH)_3 + OH^- \longrightarrow CrO_4^{2-} + 3e^-$

$Cr(OH)_3 + OH^- + 4OH^- \longrightarrow CrO_4^{2-} + 4H_2O + 3e^-$

or $Cr(OH)_3 + 5OH^- \longrightarrow CrO_4^{2-} + 4H_2O + 3e^-$

(*ii*) $IO_3^- \longrightarrow I^-$

The oxidation number of iodine on the left is +5 and on the right is –1. To account for the difference, add 6 electrons on the left.

$IO_3^- + 6e^- \longrightarrow I^-$

Other steps are :

$IO_3^- + 6e^- \longrightarrow I^- + 3OH^-$

$IO_3^- + 3H_2O + 6e^- \longrightarrow I^- + 3OH^- + 3OH^-$

or $IO_3^- + 3H_2O + 6e^- \longrightarrow I^- + 6OH^-$

Step 3. Add the two half reactions. To equate the number of electrons, multiply the oxidation half reaction by 2.

$Cr(OH)_3 + 5OH^- \longrightarrow CrO_4^{2-} + 4H_2O + 3e^-] \times 2$

$IO_3^- + 3H_2O + 6e^- \longrightarrow I^- + 6OH^-$

$2Cr(OH)_3 + IO_3^- + 4OH^- \longrightarrow 2CrO_4^{2-} + 5H_2O + I^-$

(*b*) The equation is :

$MnO_4^- + SO_3^{2-} \longrightarrow Mn^{2+} + SO_4^{2-}$ (in acidic medium)

The equation can be separated as :

Reduction : $\overset{+7}{Mn}O_4^- \longrightarrow \overset{+2}{Mn^{2-}}$

Oxidation : $\overset{+4}{S}O_3^{2-} \longrightarrow \overset{+6}{SO_4^{2-}}$

These can be balanced by following the steps as given above.

(*i*) $MnO_4^- \longrightarrow Mn^{2+}$

$MnO_4^- + 5e^- \longrightarrow Mn^{2+}$

$MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

(*ii*) $SO_3^{2-} \longrightarrow SO_4^{2-}$

$SO_3^{2-} \longrightarrow SO_4^{2-} + 2e^-$

$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2e^-$

$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2e^- + 2H^+$

(*iii*) Adding the two half reactions by equating the number of electrons

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$

$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

(*c*) $Br_2 + H_2O_2 \longrightarrow BrO_3^- + H_2O$

$\overset{0}{Br_2} + \overset{+1\ -1}{H_2O_2} \quad \overset{+5\ -2}{(BrO_3)^-} + H_2O$

Separating the equation into two half reactions :

Oxidation : $\overset{0}{Br_2} \longrightarrow \overset{+5}{BrO_3^-}$

Reduction : $\overset{-1}{H_2O_2} \longrightarrow \overset{-2}{H_2O}$

Balancing the two half reactions separately

(*i*) $\overset{0}{Br_2} \longrightarrow \overset{+5}{BrO_3^-}$

Since each Br loses 5 electrons

$Br_2 \longrightarrow 2BrO_3^- + 10e^-$

$Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 10e^-$

$Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 10e^- + 12H^+$

(*ii*) $\overset{-1}{H_2O_2} \longrightarrow \overset{-2}{H_2O}$

Each O atom gains one electron

$\overset{-1}{H_2O_2} + 2e^- \longrightarrow \overset{-2}{H_2O}$

$H_2O_2 + 2e^- \longrightarrow 2H_2O$

$H_2O_2 + 2e^- + 2H^+ \longrightarrow 2H_2O$

(*iii*) Adding the two half reactions by equating the number of electrons.

$Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 12H^+ + 10e^-$

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O] \times 5$

$Br_2 + 5H_2O_2 \longrightarrow 2BrO_3^- + 4H_2O + 2H^+$

❑ **Example 28.**

In passing chlorine gas through a concentrated solution of alkali we get chloride and chlorate ions.

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Obtain balanced chemical equation for this reaction

Solution: The chemical equation for the reaction is

$$Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$$

Separating the equation into two half reactions :

$$\overset{0}{Cl_2} + \overset{-2\ +1}{OH^-} \longrightarrow \overset{-1}{Cl^-} + \overset{+5\ -2}{ClO_3^-} + \overset{+1\ -2}{H_2O}$$

Oxidation : $\overset{0}{Cl_2} \longrightarrow \overset{+5}{ClO_3^-}$

Reduction : $\overset{0}{Cl_2} \longrightarrow \overset{-1}{Cl^-}$

Balancing the two half reactions separately,

(*i*) $\overset{0}{Cl_2} \longrightarrow \overset{+5}{ClO_3}$

Each Cl atom loses 5 electrons

$$Cl_2 \longrightarrow 2ClO_3^- + 10\,e^-$$

$$Cl_2 + 6H_2O \longrightarrow 2ClO_3^- + 10\,e^-$$

$$Cl_2 + 6H_2O + 12OH^- \longrightarrow 2ClO_3^- + 10\,e^- + 12\ H_2O$$

(*ii*) $Cl_2 \longrightarrow Cl^-$

Each Cl atom gains one electron.

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

(*iii*) Adding the two half reactions by equating the number of electrons :

$$Cl_2 + 6H_2O + 12OH^- \longrightarrow 2ClO_3^- + 12H_2O + 10e^-$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \ ] \times 5$$

$$6Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10\ Cl^- + 6H_2O$$

or $$3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$$

❑ Example 29.

Balance the following equation by oxidation number as well as ion–electron method :

$P(s) + OH^-(aq) \longrightarrow PH_3(g) + H_2PO_2^-(aq)$

Solution: (*i*) *Oxidation number method :*

1. The skeleton equation with oxidation number is

$$\overset{0}{P} + \overset{-2\ +1}{OH^-} \longrightarrow \overset{-3\ +1}{PH_3} + \overset{+1\ +1\ -2}{H_2PO_2^-}$$

O.N. increases by 1 per atom

$$\overset{0}{P} + OH^- \longrightarrow \overset{-3}{PH_3} + \overset{+1}{H_2PO_2^-}$$

O.N. decreases by 3 per atom

2. To balance increase and decrease, multiply $H_2PO_2^-$ by 3.

$$P + OH^- \longrightarrow PH_3 + 3H_2PO_2^-$$

3. To balance all atoms (other than H and O) multiply P by 4

$$4P + OH^- \longrightarrow PH_3 + 3H_2PO_2^-$$

4. To balance O atoms add OH^- ions to L.H.S.

$$4P + OH^- + 5OH^- \longrightarrow PH_3 + 3H_2PO_2^-$$

5. To balance H atoms add H_2O molecules on L.H.S. and equal number of OH^- ions on other side

$$4P + 6OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^- + 3OH^-$$

or $$4P + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$$

(*ii*) *Ion electron method*

1. Oxidation number of each atom :

$$\overset{0}{P} + OH^- \longrightarrow \overset{-3}{PH_3} + \overset{+1}{H_2PO_2^-}$$

In this P undergoes oxidation to $H_2PO_2^-$ and reduction to PH_3

Oxidation : $P \longrightarrow H_2PO_2^-$

Reduction : $P \longrightarrow PH_3$

2. Balance each reaction separately

(*a*) $\overset{+1}{P} \longrightarrow H_2PO_2^-$

(*i*) Add electron to make up the difference in oxidation number

$$P \longrightarrow H_2PO_2^- + e^-$$

(*ii*) Balance OH^- ions to balance charge

$$P + 2OH^- \longrightarrow H_2PO_2^- + e^- \quad .....(i)$$

(*b*) $\overset{0}{P} \longrightarrow \overset{-3}{PH_3}$

(*i*) Add electrons to balance oxidation state

$$P + 3e^- \longrightarrow PH_3$$

(*ii*) Add OH^- ions to balance charge

$$P + 3e^- \longrightarrow PH_3 + 3OH^-$$

(*iii*) Add $3H_2O$ molecules on L.H.S. to balance O and H atoms

$$P + 3H_2O + 3e^- \longrightarrow PH_3 + 3OH^- \quad ....(ii)$$

3. Multiply eqn (*i*) by 3 and add to eqn (*ii*)

$$4P + 3H_2O + 6OH^- \longrightarrow PH_3 + 3OH^- + 3H_2PO_2^-$$

or $$4P + 3H_2O + 3OH^- \longrightarrow PH_3 + 3H_2PO_2^-$$

❑ Example 30.

Permanganate (VII) ion, MnO_4^- in basic solution oxidises iodide ion, I^- to produce molecular iodine (I_2) and manganese (IV) oxide (MnO_2). Write a balanced ionic equation to represent this redox reaction. ***N.C.E.R.T.***

Solution: The skeleton equation for the reaction is :

$$MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_2(s) + I_2(s)$$

1. Separating the equation into two half reactions :

Oxidation : $\overset{-1}{I^-} \longrightarrow \overset{0}{I_2}$

Reduction: $\overset{+7}{MnO_4^-} \longrightarrow \overset{+4}{MnO_2}$

Balancing the two half reactions separately

(*i*) $\overset{-1}{I^-} \longrightarrow \overset{0}{I_2}$

Each I^- ion loses one electron each

$$2I^- \longrightarrow I_2 + 2e^-$$

(*ii*) $\overset{+7}{MnO_4^-} \longrightarrow \overset{+4}{MnO_2}$

$$MnO_4^- + 3e^- \longrightarrow MnO_2$$

Since the reaction occurs in basic medium, add OH^- ions on R.H.S. to balance O atoms

$$MnO_4^- + 3e^- \longrightarrow MnO_2 + 2OH^-$$

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To balance H atoms add H_2O molecules on L.H.S. and equal number of OH^- ions on the other side

$$MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 2OH^- + 2OH^-$$

Adding the two half reactions by equating the number of electrons :

$$2I^- \longrightarrow I_2 + 2e^-] \times 3$$

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-] \times 2$$

$$2MnO_4^- + 6I^- + 4H_2O \longrightarrow 2MnO_2 + 3I_2 + 8OH^-$$

A verification of this equation shows that it is balanced in respect to the number of atoms and charges on both sides.

Practice Problems

14. Balance the following equations by ion electron method :

(*a*) $NO_3^- + Bi(s) \longrightarrow Bi^{3+} + NO_2$ (in acidic medium)

(*b*) $MnO_4^- + H_2C_2O_4 \longrightarrow Mn^{2+} + CO_2$ (in acidic medium)

(*c*) $Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}$ (in acidic medium)

(*d*) $MnO_4^- + Br^- \longrightarrow Mn^{2+} + Br_2$ (in acidic medium)

(*e*) $MnO_4^- + SO_3^{2-} \longrightarrow Mn^{2+} + SO_4^{2-}$ (acidic medium)

(*f*) $Cl_2O_7(g) + H_2O_2(g) \longrightarrow ClO_2^-(aq) + O_2(g)$

15. Starting with correctly balanced half reactions, write the overall net reactions for the following changes:

(*a*) Nitrous acid (HNO_2) oxidises, I^- to I_2 in acidic medium.

(*b*) Chloride ion is oxidised to Cl_2 by MnO_4^- in acidic medium.

Answers to Practice Problems

14. (*a*) $3NO_3^- + Bi + 6H^+ \longrightarrow 3NO_2 + 3H_2O + Bi^{3+}$

(*b*) $2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

(*c*) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

(*d*) $2MnO_4^- + 10\,Br^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Br_2 + 8H_2O$

(*e*) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5\,SO_4^{2-} + 3H_2O$

(*f*) $Cl_2O_7 + 4H_2O_2 + 2OH^- \longrightarrow 2Cl_2^- + 4O_2 + 5H_2O$

15. (*a*) $2I^- + 2NO_2^- + 4H^+ \longrightarrow I_2 + 2NO + 2H_2O$

(*b*) $2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 5Cl_2 + 2Mn^{2+} + 8H_2O$

APPLICATIONS OF REDOX REACTIONS

Redox reactions are the basis of many applications in chemistry. Some of the important applications of redox reactions are :

1. Photosynthesis. Photosynthesis is used to convert carbon dioxide and water by chlorophyll of green plants in the presence of sunlight to carbohydrates.

$$6CO_2(g) + 6H_2O(l) \xrightarrow[\text{Sunlight}]{\text{Chlorophyll}} C_6H_{12}O_6(aq) + 6O_2(g)$$

In this case, CO_2 is reduced to carbohydrates and water is oxidised to oxygen. The light provides the energy required for the reaction. This reaction is a source of food for plants and animals.

2. In metallurgy. Many metal oxides are reduced to metals by using suitable reducing agents. For example, Al_2O_3 is reduced to aluminium by cathodic reduction in electrolytic cell. Fe_2O_3 is reduced to iron in a blast furnace using coke. Other metals such as magnesium, calcium, strontium, barium, sodium, potassium, etc., are produced commercially by electrolysis methods.

3. Production of chemicals. Many chemical compounds of our common need are commercially prepared by redox reactions. For example, sodium hydroxide, Cl_2, F_2, KOH, etc. are produced by electrolysis which is based on redox reactions.

4. Oxidation of fuels. Oxidation of fuels is an important source of energy which satisfies our daily need of life. These are used for obtaining energy for domestic, transport or industrial purposes. They are also used for digestion of food in animals.

$$\text{Fuels} + O_2 \longrightarrow CO_2 + H_2O + \text{Energy}$$

In living cells, glucose ($C_6H_{12}O_6$) is oxidised to CO_2 and H_2O in the presence of oxygen and energy is released.

$$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) + \text{Energy}$$

5. Electrochemical cells or batteries. The electrochemical cells or batteries are most important and are contributing significantly in different fields. They provide a source of electricity in many motors in small and large equipments. Our vehicles cars, trucks, buses, etc. are moving on the storage cells based on redox reactions. The electrochemical cells involving reaction between hydrogen and oxygen using hydrogen and oxygen electrodes in fuel cells meet our demand of electrical energy in space capsule.

6. Quantitative relationships and stoichiometry. Redox reactions also play significant role in quantitative analysis of different species by redox titrations. These titrations involve the reactions between oxidising and reducing agents and help to calculate the amount of unknown species in solutions.

REDOX TITRATIONS : REDOX REACTIONS AS THE BASIS FOR TITRATIONS

The titration of an acid with a base or of a base with an acid is very convenient method for the

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measurement of quantities of the substances in solution. The titration is carried out by adding a solution of the reagent of known concentration (standard solution) taken in a **burette** to unknown solution taken in a flask known as **titration flask**. The solution taken in a burette is called **titrant** and the other solution taken in the titration flask is called **analyte**. The titration is continued until the stoichiometric amounts of the two reagents (titrant and analyte) have been mixed. For example in a titration of a strong acid such as HCl and a strong base such as NaOH, the following reaction occurs.

$$HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l)$$

The stoichometric point corresponds to the neutralisation of HCl and NaOH. It is also called **equivalence point** or **end point.**

There are several methods for determining the equivalence point. The simplest method is to add to the solution a dye that shows change in colour at the equivalence point. Such dyes are called **indicators**. The indicator helps to determine the end point by showing change in colour. For example, when phenolphthalein is added to a basic solution, it gives pink colour. When this solution is titrated against an acid solution, the end point is indicated by disappearance of pink colour.

The same principles apply to redox titrations. However, the indicators used in acid-base titrations are not used for redox titrations. There are a number of oxidising agents such as acidified $KMnO_4$, acidified $K_2Cr_2O_7$, iodine solution, potassium iodate etc. which can be titrated against reducing agents such as ferrous suphate (or Fe^{2+} ions), oxalic acid, sodium thiosulphate, potassium iodide etc. For example :

1. Potassium permanganate titrations

Potassium permanganate, $KMnO_4$ is a versatile and strong oxidising agent used in estimation of many reducing agents such as Fe^{2+} ions, oxalates ions etc. In these titrations, no indicator is used because $KMnO_4$ is itself intensely coloured (dark purple). So, $KMnO_4$ acts as a self indicator and when it is titrated against a reducing agent (*e.g.* Fe^{2+}, $C_2O_4^{2-}$) its colour disappears. As soon as the reducing agent has been used up, the additional a single drop of potassium permanganate gives a tinge of pink colour to the solution. For example, pink colour appears at MnO_4^- concentration as low as 10^{-6} mol L^{-1}. This ensures a minimal 'overshoot' in the colour beyond the equivalence point i.e., the point where the reductant and oxidant are equal in terms of their stoichiometry.

The reaction for titration of MnO_4^- against Fe^{2+} ions is :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Similarly, the reaction for the titration of MnO_4^- against oxalate ions is

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \longrightarrow 2CO_2 + 2e^- \Big] \times 5$$

$$2MnO_4^- + 5 \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

2. Potassium dichromate titrations

Acidified potassium dichromate $K_2Cr_2O_7$ is also used as an oxidising agent in redox titrations. It is a relatively weak oxidising agent as compared to $KMnO_4$. However, unlike $KMnO_4$, it does not act as a self indicator because no dramatic auto-colour change (as with MnO_4^- titrations) occurs in these titrations. In these titrations, indicators such as diphenylamine, N–phenylanthranilic acid (and external indicator potassium ferricyanide, $K_4[Fe(CN)_6]$ are commonly used. For example, $K_2Cr_2O_7$ oxidises the indicator diphenylamine just after the equivalence point to give intense blue colour indicating the end point. The chemical equation showing $Cr_2O_7^{2-}$ as an oxidising agent is :

$$Cr_2O_7^{2-} + 14\ H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Oxidation of ferrous salts with $K_2Cr_2O_7$ may be written as:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Iodimetric and Iodometric titrations

Iodine, I_2 also acts as a mild oxidising agent in solution according to the reaction :

$$I_2 + 2e^- \longrightarrow 2I^-$$

It may be noted that iodine being nonpolar is very slightly soluble in water. However, it dissolves in water in the presence of potassium iodide due to the formation of KI_3 as :

$$KI + I_2 \rightleftharpoons KI_3$$

Iodine can be used for titrating strong reducing agents like sodium thiosulphate according to the reaction :

$$I_2\ (aq) + S_2O_3^{2-}\ (aq) \longrightarrow 2I^-\ (aq) + S_4O_6^{2-}(aq)$$

These titration in which iodine is directly titrated against a reducing agent are called ***iodimetric titrations.***

There is another method in which iodine is liberated from potassium iodide by some oxidising agent and liberated iodine is titrated against standard sodium thiosulphate solution. *These titrations in which liberated iodine from an oxidising agent is titrated against a standard solution of sodium thiosulphate* are called ***iodometric titration.*** For example, Cu^{2+} ions (*e.g.* $CuSO_4$) is estimated by oxidising I^- ions (from KI) to liberate I_2, which is titrated against $Na_2S_2O_3$.

$$2Cu^{2+}\ (aq) + 4I^-(aq) \longrightarrow Cu_2I_2(s) + I_2\ (aq)$$
$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

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In these iodine titrations, end point can be detected by adding freshly prepared starch solution. It reacts with iodine in the presence of iodide to form intensely blue coloured complex. Iodine appearance or disappearance can be identified very sharply by this method.

STOICHIOMETRY OF REDOX REACTIONS

The quantitative relationships between different chemical species in redox reactions are derived exactly in the same way as discussed in Unit 1 for general chemical reactions. To perform stoichiometric calculations, we need a balanced redox equation for the reaction because the coefficients in the equation tell us the ratio by moles in which the reactants combine and in which the products are formed. If we know the molarities of the reductant and oxidant and their volumes used in titration and n_1 and n_2 are their stoichiometric coefficients, then molarity equation may be written as :

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$ for volumetric estimation.

For example, in the titration of $FeSO_4$ with $KMnO_4$, the balanced equation is :

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

If $FeSO_4$ is considered as reagent 1 and $KMnO_4$ is reagent 2, then molarity equation becomes :

$$\frac{M_1V_1}{10} = \frac{M_2V_2}{2}$$

or $$\frac{M_1V_1}{5} = \frac{M_2V_2}{1}$$

This relation can be used to calculate unknown quantity if other three quantities are known.

It may be noted that normality equation can also be used to determine the stoichiometry of redox reactions. The normality equation is

$$N_1V_1 \equiv N_2V_2$$

If we know the normality (N_1) of any solution of an oxidising agent and volume (V_1) of this solution which completely oxidises the known volume (V_2) of the solution of a reducing agent then normality of reducing agent can be calculated or vice-versa.

Once the normality of the reducing (or the oxidising) agent is known, its strength can be calculated as :

Strength = Normality of the solution × Equivalent weight of the oxidising (or the reducing) agent.

However, it may be noted that molarity equation is preferred over normality equation. *The basic rules for calculations are same as discussed in Unit 1.*

The main important step is to write the balanced redox equation.

SOLVED EXAMPLES

Example 31.

How many grams of potassium dichromate are required to oxidise 20.0 g of Fe^{2+} in $FeSO_4$ to Fe^{3+} if the reaction is carried out in an acidic solution ?

Solution: When dissolved in water, $K_2Cr_2O_7$ dissociates into K^+ and $Cr_2O_7^{2-}$ ions and $FeSO_4$ dissociates into $Fe^{2+}$and SO_4^{2-} ions. The skeleton equation is :

$$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + 2Cr^{3+}$$

The balanced equation is

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

From the balanced equation, it is clear that

$$1 \text{ mol } K_2Cr_2O_7 \equiv 6 \text{ mol } FeSO_4$$

Formula weight of $K_2Cr_2O_7 = 2 \times 39 + 2 \times 52 + 7 \times 16 = 294$

Formula weight of $FeSO_4 = 56 + 32 + 4 \times 16 = 152$

$\therefore$ 1 mol $K_2Cr_2O_7$ ≡ 6 mol $FeSO_4$

294 6 × 152

6 × 152 g of $FeSO_4$ require $K_2Cr_2O_7$ = 294 g

20 g of $FeSO_4$ require $K_2Cr_2O_7 = \frac{294}{6 \times 152} \times 20 = \mathbf{6.45\ g}$

$K_2Cr_2O_7$ required to oxidise 20 g of $FeSO_4$ = **6.45 g**

Example 32.

How many millilitres of 0.125 M $KMnO_4$ are required to react completely with 25.0 mL of 0.250 M $FeSO_4$ solution in the acidic medium ?

Solution: The balanced chemical equation is :

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

From the balanced equation, it is clear

1 mol $KMnO_4$ = 5 mol $FeSO_4$

158 5 × 152

Moles of $FeSO_4$ present in 25 mL of 0.250 M solution :

$$= \frac{0.250}{1000} \times 25 = 0.00625 \text{ mol}$$

Let us determine the number of moles of $KMnO_4$ that must react

5 mol of $FeSO_4$ react with $KMnO_4$ = 1 mol

0.00625 mol of $FeSO_4$ will react with $KMnO_4$

$$= \frac{1}{5} \times 0.00625 = 0.00125 \text{ mol}$$

Now, we are to calculate the volume of 0.125 M $KMnO_4$ solution which contain 0.00125 mol.

According to definition of molarity, 0.125 M solution means that

0.125 mol of $KMnO_4$ is present in = 1000 mL

0.00125 mol of $KMnO_4$ is present in

$$= \frac{1000}{0.125} \times 0.00125 = 10 \text{ mL}$$

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This can also be calculated as :

$$\text{Molarity} = \frac{\text{Moles} \times 1000}{\text{Volume}}$$

$$0.125 = \frac{0.00125 \times 1000}{\text{Volume}}$$

$$\therefore \quad \text{Volume} = \frac{0.00125 \times 1000}{0.125} = 10 \text{ mL}$$

❑ **Example 33.**

How many millilitres of 0.025 M $K_2Cr_2O_7$ are required to react completely with 25.0 mL of 0.20 M solution of $FeSO_4$?

Solution: The balanced chemical equation is

$$6Fe^{2+} + 6Cr_2O_7^{2} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

1 mol of $K_2Cr_2O_7 \equiv$ 6 mol of $FeSO_4$

Moles of $FeSO_4$ present in 25.0 mL of 0.20 M solution

$$\frac{0.20}{1000} \times 25.0 = 0.005 \text{ mol}$$

Now 6 mol of $FeSO_4$ require $K_2Cr_2O_7$

$$= 1 \text{ mol}$$

$$= \frac{1}{6} \times 0.005 = 0.000833 \text{ mol}$$

Let us calculate the volume of $K_2Cr_2O_7$ solution containing 0.000833 mol

0.025 mol of $K_2Cr_2O_7$ are present in

$$= 1000 \text{ mL}$$

0.000833 mol of $K_2Cr_2O_7$ are present in

$$= \frac{1000 \times 0.000833}{0.025} = \mathbf{33.3\ mL}$$

❑ **Example 34.**

Determine the volume of $\frac{M}{10}$ $KMnO_4$ solution required to react completely with 25.0 mL of M/5 oxalic acid solution.

Solution: The balanced chemical equation is

$$2KMnO_4 + 5(COOH)_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

From the balanced equation, it is clear that

2 mol of $KMnO_4 \equiv$ 5 mol of $(COOH)_2$

Applying molarity equation

$$\left[\frac{M_1V_1}{n_1}\right]_{KMnO_4} \equiv \left[\frac{M_2V_2}{n_2}\right]_{(COOH)_2}$$

$$\frac{1}{10} \times \frac{V_1}{2} = \frac{1}{5} \times \frac{25.0}{5}$$

$$\text{or } V_1 = \frac{25.0 \times 10 \times 2}{5 \times 5} = \mathbf{20.0\ mL}.$$

❑ **Example 35.**

1.80 g of impure sample of oxalate was dissolved in water and the solution made to 250 mL. On titration 20 mL of this solution required 30 mL of M/50 $KMnO_4$ solution. Calculate the percentage purity of the sample.

Solution: The balanced chemical equation is :

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Applying molarity equation,

$$\left(\frac{M_1V_1}{n_1}\right)_{KMnO_4} \equiv \left(\frac{M_2V_2}{n_2}\right)_{C_2O_4^{2-}}$$

$$\frac{1}{50} \times \frac{30}{2} \equiv \frac{M_2 \times 20}{5}$$

$$M_2 = \frac{30 \times 5}{50 \times 2 \times 20} = 0.075 \text{ M}$$

Molecular wt. of $C_2O_4^{2-} = 88$

Wt. of $C_2O_4^{2-} = 0.075 \times 88 = 6.6$ g

Amount of $C_2O_4^{2-}$ in 250 mL = $\frac{6.6}{1000} \times 250 = 1.65$g

$$\% \text{ Purity} = \frac{1.65}{1.80} \times 100 = 91.7\%$$

❑ **Example 36.**

2.48 g of hydrated sodium thiosulphate ($Na_2S_2O_3 \cdot xH_2O$) was dissolved per litre of the solution. 25 mL of this solution required 12.5 mL of M/100 iodine solution. Determine the value of x.

Solution: The balanced chemical equation is :

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

Let the molarity of $Na_2S_2O_3 \cdot xH_2O$ be M_1

Applying molarity equation,

$$\left(\frac{M_1V_1}{n_1}\right)_{Na_2S_2O_3} \equiv \left(\frac{M_2V_2}{n_2}\right)_{I_2}$$

$$\frac{M_1 \times 25}{2} \equiv \frac{1}{100} \times \frac{12.5}{1}$$

$$M_1 = \frac{12.5 \times 2}{100 \times 25} = 0.01 \text{ M}$$

Molecular wt. of $Na_2S_2O_3 \cdot xH_2O$

$$= 2 \times 23 + 2 \times 32 + 3 \times 16 + x \times 18$$

$$= 158 + 18x$$

Amount of $Na_2S_2O_3 \cdot xH_2O = 0.01 \times (158 + 18x)\ g$

But actual amount = 2.48 *g*

$\therefore$ $0.01(158 + 18x) = 2.48$

$$(158 + 18x) = \frac{2.48}{0.01} = 248$$

$$18x = 248 - 158 = 90$$

$$\therefore \quad x = \frac{90}{18} = \mathbf{5}.$$

Practice Problems

◑ **16.** How many millilitres of 0.125 M $K_2Cr_2O_7$ are required to react completely with 25.0 mL of 0.250 M $FeSO_4$ solution in acidic medium?

◑ **17.** A 16.4 ml volume of 0.14 M $KMnO_4$ solution is required to oxidise 20.0 ml of $FeSO_4$ solution in acidic medium. What is the concentration of $FeSO_4$ solution ?

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18. How many millilitres of 0.150 M $KMnO_4$ solution are required to react completely with 35.0 ml of 0.150 M $SnCl_2$ solution, given the chemical equation for the reaction :

$5\ Sn^{2+} + 2\ MnO_4^- + 16H^+ \rightarrow\ 5\ Sn^{4+} + 2Mn^{2+} + 8H_2O$

19. Calculate the concentration of hypo ($Na_2S_2O_3 \cdot 5H_2O$) solution in gL^{-1} if 10.0 mL of this solution decolourised 25 mL of M/50 iodine solution.

20. Calculate the volume of 0.05 M $KMnO_4$ solution required to completely oxidise 3.20 g of oxalic acid ($H_2C_2O_4$) in acidic medium.

Answers to Practice Problems

16. The balance equation is

$6Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

From the equation, it is clear

$$\left(\frac{M_1V_1}{n_1}\right) K_2Cr_2O_7 \equiv \left(\frac{M_2V_2}{n_2}\right) FeSO_4$$

$$\frac{0.125 \times V_1}{1} = \frac{0.250 \times 25.0}{6}$$

$$\therefore\ V_1 = \frac{0.250 \times 25.0}{0.125 \times 6} = \mathbf{8.33\ mL}$$

17. $MnO_4^- + 5Fe^{2+} + 8\ H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{5}$$

$$\text{or}\quad \frac{0.14 \times 16.4}{1} = \frac{20.0 \times M_2}{5}$$

$$\therefore\ M_2 = \frac{0.14 \times 16.4 \times 5}{20.0} = \mathbf{0.574\ mL}$$

18. $5Sn^{2+} + 2MnO_4^- + 16\ H^+ \longrightarrow 5Sn^{4+} + 2Mn^{2+} + 8\ H_2O$

$$\frac{M_1V_1}{5} = \frac{M_2V_2}{2}$$

$$\text{or}\quad \frac{35.0 \times 0.150}{5} = \frac{0.150 \times V_2}{2}$$

$$\therefore\ V_2 = \frac{35.0 \times 0.150 \times 2}{0.150 \times 5} = \mathbf{14.0\ mL}.$$

19. $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

$$\frac{M_1 \times 10}{2} = \frac{1}{50} \times \frac{25}{1} \text{ or } M_1 = 0.1\ M$$

Conc. of $Na_2S_2O_3 \cdot 5H_2O$ = $0.1 \times 248 = 24.8\ gL^{-1}$.

20. $2KMnO_4 + 5(COOH)_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

Moles of oxalic acid = $\frac{3.25}{90} = 0.035$

5 moles of $(COOH)_2 \equiv$ 2 moles of $KMnO_4$

0.035 moles of $(COOH)_2 = \frac{2}{5} \times 0.035 = 0.014$ mol.

Now, 0.05 mol of $KMnO_4$ is present in solution = 1000 mL.

$\therefore$ 0.014 mol of $KMnO_4$ is present in solution

$$= \frac{1000}{0.05} \times 0.014 = \mathbf{280\ mL}.$$

INDIRECT REDOX REACTIONS: ELECTROCHEMICAL CELLS

In the direct redox reaction, the transference of electrons is limited to very small distances and, therefore, no useful electrical work could be obtained. In these reactions, chemical energy appears as *heat*. However, if the transference of electrons from zinc to copper ions is allowed to occur through some metallic wires, useful electrical work could be performed. Such redox reactions are called indirect redox reactions and electrical energy is produced during such spontaneous reactions instead of heat energy. Let us consider the above redox reaction between Zn metal and Cu^{2+} ions performed indirectly in separate vessels.

The arrangement consists of two beakers, one of which contains 1.0 M solution of zinc sulphate and the other 1.0 M solution of copper sulphate. A zinc rod is dipped into $ZnSO_4$ solution while a copper rod is dipped into $CuSO_4$ solution. *These rods are known as* **electrodes**. The metallic rods in the beaker are connected to the ammeter by means of an insulated wire through a key having an on or off switch. The solutions in the two beakers are connected by an inverted U-tube containing concentrated aqueous solution of some electrolyte such as KCl, KNO_3, or NH_4NO_3 *which does not undergo a chemical change during the* process. The two openings of the U-tube are plugged with some porous material such as glass wool or cotton (Fig. 3). The U-tube which connects the two glass beakers is called a **salt bridge.** Its function will be discussed separately.

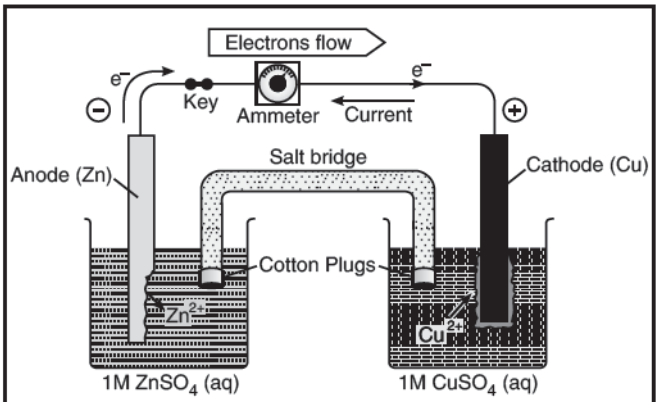

Fig. 3. Indirect redox reaction between zinc and copper sulphate.

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When the switch is in the off position, no reaction takes place in either of the beakers and no current flows through the metallic wire. When the switch is in the on position, the following observations can be made :

(*i*) There is a flow of electric current through the external circuit.

(*ii*) The zinc rod loses its weight and the copper plate gains weight.

(*iii*) The concentration of $ZnSO_4$ solution increases and that of $CuSO_4$ solution decreases.

(*iv*) The solutions in the two beakers remain electrically neutral.

From these observations, it is clear that the overall reaction is :

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

During the reaction, zinc is oxidised to Zn^{2+} ions which go into the solution. The electrons released

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

at the electrode move towards the other electrode through outer circuit. These electrons are accepted by Cu^{2+} ions of $CuSO_4$ solution which are reduced to copper. The metal gets deposited on the copper electrode.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

Thus, zinc plate gradually loses its weight while copper plate gains in weight.

The redox reaction occurring in this indirect arrangement is the same as that taking place in a single beaker. The basic difference between the two is that in *the direct redox reaction, energy is liberated in the form of heat energy whereas in indirect redox reaction, energy is liberated in the form of electrical energy.* Thus, indirect redox reactions lead to the production of electrical energy. The arrangement for carrying out indirect redox reactions is called electrochemical cell. Thus, an **electrochemical cell** is

a device used to convert chemical energy produced in a redox reaction into electrical energy.

The electrochemical cells are also called **galvanic cells** or **voltaic cells** after the names of the scientists Luigi Galvani (1780) and Alessandro Volta (1800) who were the first to device such experiments for converting chemical energy into electrical energy.

Salt Bridge and its Functions

A salt bridge has an important role to play in an electrochemical cell. It is usually an inverted U- tube filled with concentrated solution of *inert electrolytes* (Fig 4). An inert electrolyte is the one whose ions are

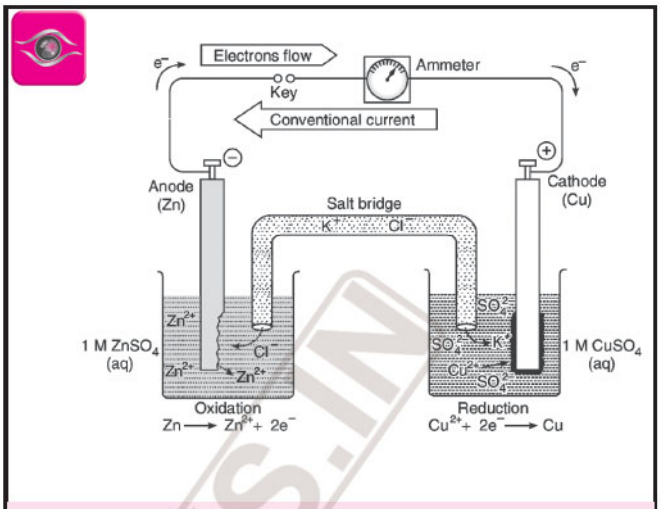

Fig. 4. Working of an electrochemical cell.

neither involved in any electrochemical change nor do they react chemically with the electrolytes electrically connected by them. Generally salts like KCl, KNO_3, NH_4NO_3, etc. are used. For preparing a salt bridge, gelatin or agar agar is dissolved in a hot aqueous solution of KCl, KNO_3 or NH_4NO_3 and filled in a U-tube. On cooling, the agar agar solution becomes solid and is used as salt bridge.

The important **functions** of the salt bridge are :

(*i*) **Salt bridge connects the solutions in the two half cells and completes the cell circuit.** For the flow of electric current through the circuit, we know that there should not be broken contacts throughout the circuit. As already explained, the solutions of the half cells are connected by a salt bridge and their electrodes by means of a wire. Therefore, the salt bridge completes the circuit.

(*ii*) **Salt bridge keeps the solutions in the two half cells electrically neutral.** In order to understand this, let us consider Zn–$CuSO_4$ cell. In the oxidation half cell, zinc atoms lose electrons and change into Zn^{2+} ions. The positively charged Zn^{2+} ions pass into the solution. After some time, this results into accumulation of extra positive charge in the solution around the anode. Similarly, in the reduction half cell, Cu^{2+} ions accept electrons and get reduced to Cu. After some time, the solution around cathode will acquire extra negative charge due to excess of SO_4^{2-} ions. The accumulation of positive charge around zinc rod will prevent the further flow of electrons from the zinc rod. Similarly, the accumulation of negative charge around copper electrode will prevent the flow of electrons to the copper ions. Thus, in the absence of salt bridge the flow of electrons will occur only momentarily and the cell will stop working.

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However, the accumulation of charges in the two half cells is prevented by using a salt bridge. When the concentration of Zn^{2+} ions around anode increases, sufficient number of Cl^- ions migrate from the salt bridge to the anode half cell. Similarly, to neutralise the excess negative charge due to the additional SO_4^{2-} ions in cathode half cell, sufficient number of K^+ ions migrate from the salt bridge to this half cell. Thus, the salt bridge provides cations and anions to replace the ions lost or produced in the two half cells to maintain electrical neutrality.

It may be noted that the salt bridge in a cell can be replaced by a *porous partition* which allows the migration of ions without allowing the solutions to intermix.

The working of the electrochemical cell is represented in Fig. 4.

Half Cells and Half Cell Reactions

In the indirect redox reactions, the oxidation and reduction occur separately and these are called **half cells.** The reactions occurring in half cells are called **half cell reactions**. The half cell in which oxidation (loss of electrons) occurs is called **oxidation half cell** and the reaction taking place in it is called **oxidation half cell reaction**. Similarly, half cell in which reduction (gain of electrons) occurs is called **reduction half cell** and the reaction taking place in it is called **reduction half cell reaction**. The two half cells constitute a *redox couple. A redox couple* is defined *as having together the oxidized and reduced forms of a substance taking part in an oxidation or reduction half reaction.*

The net reaction is the sum of two half cell reactions. This can be illustrated by the following examples :

Reaction between Zn metal and Cu^{2+} ions ($CuSO_4$ solution) may be written as :

Oxidation half reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Net reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Similarly, in case of aluminium metal displacing silver ions from a solution of silver nitrate we get the half reactions as :

Oxidation half reaction: $Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$

Reduction half reaction: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

To balance the number of electrons, we multiply reduction half reaction by 3 and then add so that net reaction becomes

$$Al(s) + 3Ag^+(aq) \longrightarrow Al^{3+}(aq) + 3Ag(s)$$

Similarly, reaction between Cu metal and Ag^+ ions ($AgNO_3$ solution) may be written as :

Oxidation half reaction: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Reduction reaction: $2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

Net reaction: $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

The electrons lost in the oxidation half reaction must be equal to the electrons gained in the reduction half reaction. In order to equate them, the ionic equations may be multiplied suitably if necessary.

SOLVED EXAMPLES

Example 37.

Write the half reactions for the following redox reactions :

(a) $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

(b) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

(c) $Al(s) + 3Ag^+(aq) \longrightarrow Al^{3+}(aq) + 3Ag(s)$

Solution:

(a) $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

Oxidation half reaction :

$2I^-(aq) \longrightarrow I_2(aq) + 2e^-$

Reduction half reaction :

$2Fe^{3+}(aq) + 2e^-(aq) \longrightarrow 2Fe^{2+}(aq)$

(b) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

Oxidation half reaction :

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half reaction :

$2H^+(aq) \longrightarrow H_2(g)$

(c) $Al(s) + 3Ag^+(aq) \longrightarrow Al^{3+}(aq) + 3Ag(s)$

Oxidation half reaction :

$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$

Reduction half reaction :

$3Ag^+(aq) \longrightarrow 3Ag(s)$

REPRESENTATION OF AN ELECTROCHEMICAL CELL

We have seen that an electrochemical cell or galvanic cell consists of two electrodes *i.e.*, anode and cathode. The electrolyte solutions containing these electrodes are called *half cells.* When these two half cells are combined, a cell is formed. The following **universally accepted conventions** are used for representing an electrochemical cell.

1. A galvanic cell is represented by writing the anode (where oxidation occurs) on the left hand side and cathode (where reduction occurs) on the right hand side.

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2. The anode of the cell is represented by writing metal first and then the electrolyte. The two are separated either by a semicolon (;) or by a vertical line. The electrolyte may be written as ionic species or by the formula of the whole compound. For example,

$$Zn\ ;\ Zn^{2+} \quad \text{or} \quad Zn\ |\ Zn^{2+}$$

For further information, the concentration of the electrolyte is also mentioned within bracket after the cation, *i.e.,*

$$Zn\ ;\ Zn^{2+}\ (1\ M) \quad \text{or} \quad Zn\ |\ Zn^{2+}\ (1\ M)$$

In case of gas electrodes such as hydrogen electrode, inert metal which serves as the electric contact for the electrode is also written as :

$$Pt,\ H_2\ (1\ atm);\ H^+\ (1\ M)$$

In this case, Pt, H_2 (1 atm) stands for hydrogen and platinum together as solid phase, in which H_2 is absorbed under 1 atm pressure. Comma is used to indicate that they form one phase.

3. The cathode of the cell is represented by writing the electrolyte first (or cation of the electrolyte) and then metal. For example,

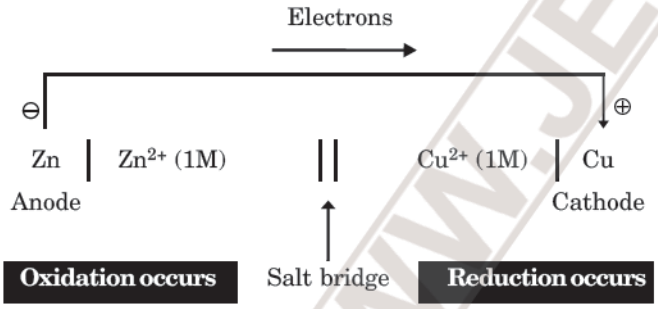
$$Cu^{2+}\ ;\ Cu \quad \text{or} \quad Cu^{2+}\ |\ Cu \quad \text{or} \quad Cu^{2+}\ (1\ M)\ |\ Cu$$

$$Cl^-\ (0.1\ M);\ Cl_2\ (1\ atm),\ Pt$$

4. The salt bridge which separates the two half cells is indicated by two vertical lines. For example,

$$Zn\ |\ Zn^{2+}\ (1M)\ \|\ Cu^{2+}\ (1M)\ |\ Cu$$

The complete formula of a cell may be represented as follows :



Sometimes negative and positive signs are also put on the electrodes. Anode is a negative pole while cathode acts as positive pole. The electrons flow from the negative pole (anode) to the positive pole (cathode) in the external circuit. On the other hand, conventionally, the current is said to flow in the opposite direction.

The important generalisations in an electrochemical cell may be summed up as :

Oxidation occurs at anode.

Reduction occurs at cathode.

Cathode is positive and anode is **negative** in a galvanic cell.

Electrons flow from **anode** to **cathode** in the external circuit.

Chemical energy is converted into **electrical energy**.

ELECTRODE POTENTIAL

When an electrode say copper, is immersed in contact with a solution of its ions, then either of the following three possibilities can take place :

(*a*) The metal ions (Cu^{2+}) may collide with the electrode and do not undergo any change.

(*b*) Cu^{2+} ions may collide with the electrode, gain electrons and get converted into metal atoms *(i.e., the ions are reduced).*

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{(Reduction)}$$

(*c*) Cu atoms on the electrode may lose electrons to the electrode and become Cu^{2+} ions and go into the solution.

$$Cu \longrightarrow Cu^{2+} + 2e^- \ \text{(Oxidation)}$$

These possibilities are shown in Fig. 5.

Now, if the metal has *relatively high tendency to get oxidised,* its atoms will lose electrons readily and form Cu^{2+} ions, which go into the solution. The

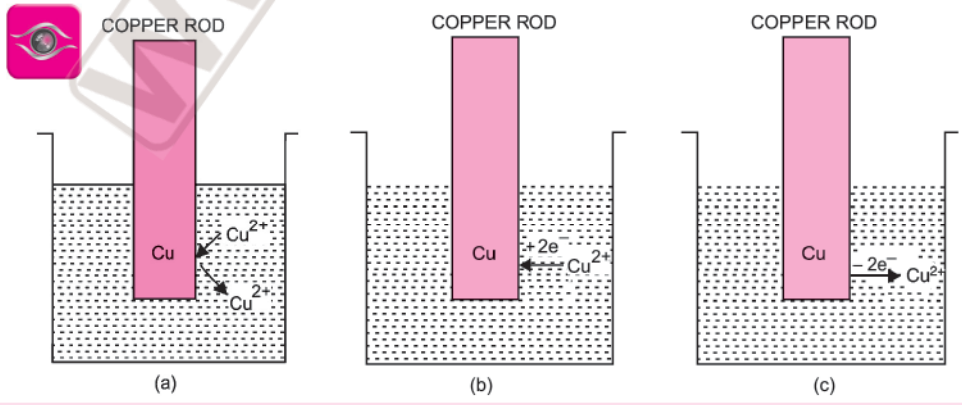


Fig. 5. Concept of electrode potential.

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electrons lost on the electrode would be accumulated on the metal electrode and the electrode acquires a slight negative charge with respect to the solution. Some of the Cu^{2+} ions from the solution will take up electrons and become Cu atoms. After some time, an equilibrium will be established as :

$$\underset{\text{Electrode}}{Cu\,(s)} \rightleftharpoons \underset{\text{Solution}}{Cu^{2+}} + \underset{\text{(on electrode)}}{2e^-}$$

When such an equilibrium is attained, it results in separation of charges (negative on the electrode with respect to the solution).

Similarly, if the metal ions have *relatively greater tendency to get reduced,* they will take electrons from the electrode. As a result, a net positive charge will be developed on the electrode with respect to the solution. This will also result into separation of charges (positive on the electrode with respect to the solution).

Due to separation of charges between the electrode and the solution, an electrical potential is set up between metal electrode and its solution. *The electrical potential difference set up between the metal and its solution* is known as **electrode potential.** Thus, the electrode potential is a measure of tendency of an electrode in a half cell to gain or lose electrons. The electrode potential may be of two types :

***(i)* Oxidation potential.** *The tendency of an electrode to lose electrons or to get oxidised* is called its **oxidation potential.** Thus, oxidation potentials give the tendency of an electrode to lose electrons, *i.e.*,

$$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$$

e.g.,

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$$

$$H_2 \rightleftharpoons 2H^+(aq) + 2e^-$$

***(ii)* Reduction potential.** *The tendency of an electrode to gain electrons or to get reduced* is called its **reduction potential.** Therefore, it measures the tendency of an electrode to gain electrons *i.e.*,

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

e.g.,

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

It is evident that the oxidation potential is the reverse of reduction potential. For example, if reduction potential of Zn is – 0.76 volts, its oxidation potential is + 0.76 volts.

According to the present convention, the half cell reactions are always written as **reduction half reactions** and their potentials are represented as **reduction potentials.**

The electrode potential depends upon

(*i*) *the nature of the metal and its ions*

(*ii*) *concentration of the ions in the solution and*

(*iii*) *temperature.*

Since the potential depends upon the concentration of the ions in solution we adopt a standard as *1 mole of ions per litre of solution.* This is called **standard electrode potential.**

The absolute value of the electrode potential cannot be determined experimentally because neither the oxidation nor the reduction reaction can occur by itself. This difficulty can be solved by selecting one of the electrodes as a reference electrode and arbitrarily fixing the potential of this electrode as **zero.** For this purpose, reversible hydrogen electrode has been universally accepted as reference electrode. It is called *standard hydrogen electrode* (S.H.E.) or *normal hydrogen electrode* (N.H.E.).

Standard Hydrogen Electrode

It consists of platinum wire sealed in a glass tube and has a platinum foil attached to it.

The foil is coated with finely divided platinum and acts as platinum electrode. It is dipped into an acid solution containing H^+ ions in 1 M concentration (1 M HCl). Pure hydrogen gas at 1 atmospheric pressure is constantly bubbled into the solution at constant temperature of 298 K. The surface of the foil acts as a site for the reaction.

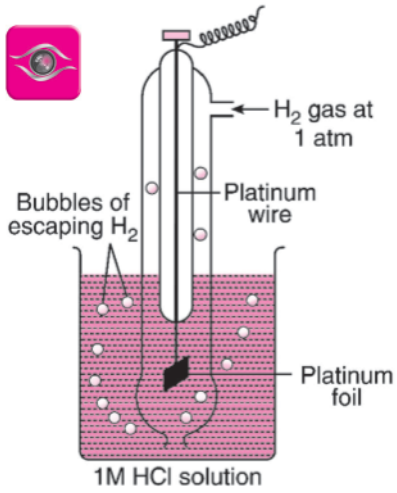

Fig. 6. Standard hydrogen electrode.

The following reactions occur in this half cell depending upon whether it acts as an anode or as a cathode.

If **S.H.E. acts as anode**

$$H_2(g) \longrightarrow 2H^+ + 2e^-$$

If **S.H.E. acts as cathode**

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

The standard hydrogen electrode is also regarded as a reversible electrode.

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$$H_2(g) \rightleftharpoons 2H^+ + 2e^-$$

The electrode potential of an electrode can be determined by connecting its half cell with a *standard hydrogen electrode*. The electrode potential of the standard hydrogen electrode is assigned **zero electrode potential.** *The electrode potential of a metal electrode as determined with respect to a standard or normal hydrogen electrode* is called **electrode potential (E).** If the concentration of the ions is 1 mol L^{-1} solution, the electrode potential is also called **standard electrode potential (E°).**

Standard hydrogen electrode is represented as : Pt, $H_2(g)$ | H^+ (aq) and has zero potential at all temperatures.

E.M.F. OR CELL POTENTIAL OF A CELL

As discussed earlier, an electrochemical cell consists of two half cells. One of the electrodes in a half cell has a higher value of reduction potential as compared to the other. As a result of this potential difference, there is a flow of electrons from the electrode with a lower reduction potential (or higher oxidation potential) to the electrode with higher reduction potential (or lower oxidation potential). *The difference between the electrode potentials of the two electrodes constituting an elecrochemical cell* is known as **electromotive force** or **cell potential** *of a cell*.

The electromotive force is commonly abbreviated as E.M.F. and is expressed in volts. The E.M.F. of a cell may be expressed in terms of the difference in the reduction electrode potential as :

$$\text{E.M.F.} = E_{\text{substance reduced}} - E_{\text{substance oxidised}}$$
$$= E_R - E_L$$

$$\text{or E.M.F.} = E_{\text{cathode}} - E_{\text{anode}}$$

where E_R and E_L represent electrode potential of electrode on right hand side and electrode on left hand side respectively. It depends upon the nature of the electrodes and the concentrations of the solutions in the two half cells. For example, the E.M.F. of a Daniell cell in which the concentrations of aqueous solutions of $CuSO_4$ and $ZnSO_4$ in the two half cells is 1 M at 298 K is 1.10 volts.

It may be noted that it is not possible to measure experimentally the absolute value of a single electrode because a half cell reaction cannot take place independently. We can measure only the difference between the electrode potentials of any two half cell reactions. Then, a question arises as to how we can obtain the reduction potential of any single electrode. Now, if the cell potential and the electrode potential for one of the half cell reactions were known, the electrode potential of the other electrode can be calculated. To solve the problem, therefore, a standard hydrogen electrode has been chosen and it has been assigned a standard reduction potential of zero volts. All other half cell reactions can be compared with this standard and a set of E° values is obtained.

- *In case, the electron accepting tendency of the metal electrode is more than that of a S.H.E., its standard reduction potential gets a* **positive sign**
- *In case the electron accepting tendency of the metal electrode is lesser than that of S.H.E. its standard reduction potential gets a* **negative sign.** It must be remembered that according to latest convention, **all standard potentials are taken as reduction potentials**.

The electrode at which **reduction** occurs with respect to S.H.E. (*i.e.*, weaker reducing agent than H^+/H_2 couple) has **+ve reduction potential.**

The electrode at which **oxidation** occurs with respect to S.H.E. (*i.e.*, stronger reducing agent than H^+/H_2 couple) has – **ve reduction potential.**

The standard electrode potentials are very important and give a lot of useful information. The basic point regarding the series is the stability of oxidized form or reduced form. *If the standard electrode potential is more than zero, then its reduced form will be more stable compared to hydrogen gas. In other words, it will be readily reduced in comparison to hydrogen and therefore, acts as strong* **oxidizing agent.** *On the other hand; if the standard electrode potential is negative than hydrogen, then hydrogen gas is more stable than the reduced form of the species. In other words, it will be readily oxidized in comparison to hydrogen and therefore, acts as* **strong reducing agent.** Similarly, we can compare two species. The species having higher electrode potential will be readily reduced (acts as oxidising agent) in comparison to the other.

ELECTROCHEMICAL SERIES

In the previous section, we have discussed the measurement of the standard reduction potentials (E°) of a few electrodes. In a similar manner, the E° values of other electrodes can also be measured. When the standard reduction potentials of the electrodes are arranged in an increasing order, a series called **electrochemical series** is obtained.

The arrangement of elements in order of decreasing reduction potential values is called **electrochemical series.**

The electrochemical series, also **called activity series**, of some typical electrodes is given in Table 1.

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Table 1. Standard reduction electrode potentials at 298 K.

Electrode		Electrode reaction (Oxidized form + ne^- ⟶ Reduced form)		E° (V)
$F_2 \mid F^-$	Strongest oxidizing agent	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	Weakest reducing agent	2.87
$Co^{3+} \mid Co^{2+}$		$Co^{3+} + e^- \longrightarrow Co^{2+}$		1.81
$H_2O_2 \mid H_2O$		$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$		1.78
$MnO_2, H^+ \mid Mn^{2+}$		$MnO_2(s) + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$		1.61
$Au^{3+} \mid Au$		$Au^{3+} + 3e^- \longrightarrow Au(s)$		1.50
$MnO_4^- \mid Mn^{2+}$		$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$		1.49
$Cl_2 \mid Cl^-$		$Cl_2(g) + 2e^- \longrightarrow 2Cl^-$		1.36
$Cr_2O_7^{2-}, H^+ \mid Cr^{3+}$		$Cr_2O_7^{2-} + 4H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$		1.33
$O_2, H^+ \mid H_2O$		$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$		1.23
$Br_2 \mid Br^-$		$Br_2(l) + 2e^- \longrightarrow 2Br^-$		1.09
$NO_3^-, H^+ \mid NO$		$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$		0.97
$Hg^{2+} \mid Hg_2^{2+}$		$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$		0.92
$ClO^- \mid Cl^-$		$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$		0.89
$Hg^{2+} \mid Hg$		$Hg^{2+} + 2e^- \longrightarrow Hg$		0.85
$Ag^+ \mid Ag$		$Ag^+ + e^- \longrightarrow Ag$		0.80
$Hg_2^{2+} \mid Hg$		$Hg_2^{2+} + e^- \longrightarrow 2Hg$		0.79
$Fe^{3+} \mid Fe^{2+}$		$Fe^{3+} + e^- \longrightarrow Fe^{2+}$		0.78
$MnO_4^- \mid MnO_4^{2-}$		$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$		0.56
$I_2 \mid I^-$		$I_2 + 2e^- \longrightarrow 2I^-$		0.54
$Cu^+ \mid Cu$		$Cu^+ + e^- \longrightarrow Cu$		0.52
$Cu^{2+} \mid Cu$		$Cu^{2+} + 2e^- \longrightarrow Cu$		0.36
$AgCl \mid Ag$		$AgCl + e^- \longrightarrow Ag + Cl^-$		0.22
$Cu^{2+} \mid Cu^+$		$Cu^{2+} + e^- \longrightarrow Cu^+$		0.15
$AgBr \mid Ag$		$AgBr + e^- \longrightarrow Ag + Br^-$		0.10
$H^+ \mid H_2$		$2H^+ + 2e^- \longrightarrow H_2$		0.00
$Fe^{3+} \mid Fe$		$Fe^{3+} + 3e^- \longrightarrow Fe$		–0.04
$Pb^{2+} \mid Pb$		$Pb^{2+} + 2e^- \longrightarrow Pb$		–0.13
$Sn^{2+} \mid Sn$		$Sn^{2+} + 2e^- \longrightarrow Sn$		–0.16
$Ni^{2+} \mid Ni$		$Ni^{2+} + 2e^- \longrightarrow Ni$		–0.25
$Fe^{2+} \mid Fe$		$Fe^{2+} + 2e^- \longrightarrow Fe$		–0.44
$Cr^{3+} \mid Cr$		$Cr^{3+} + 3e^- \longrightarrow Cr$		–0.74
$Zn^{2+} \mid Zn$		$Zn^{2+} + 2e^- \longrightarrow Zn$		–0.76
$Al^{3+} \mid Al$		$Al^{3+} + 3e^- \longrightarrow Al$		–1.66
$Mg^{2+} \mid Mg$		$Mg^{2+} + 2e^- \longrightarrow Mg$		–2.36
$Ce^{3+} \mid Ce$		$Ce^{3+} + 3e^- \longrightarrow Ce$		–2.48
$Na^+ \mid Na$		$Na^+ + e^- \longrightarrow Na$		–2.71
$Ca^{2+} \mid Ca$		$Ca^{2+} + 2e^- \longrightarrow Ca$		–2.87
$Ba^{2+} \mid Ba$		$Ba^{2+} + 2e^- \longrightarrow Ba$		–2.91
$Cs^+ \mid Cs$		$Cs^+ + e^- \longrightarrow Cs$		–2.92
$K^+ \mid K$	Weakest oxidizing agent	$K^+ + e^- \longrightarrow K$	Strongest reducing agent	–2.93
$Li^+ \mid Li$		$Li^+ + e^- \longrightarrow Li$		–3.05

STRENGTH OF OXIDIZING AGENT ↑ INCREASING

STRENGTH OF REDUCING AGENT ↓ INCREASING

It may be noted that the standard oxidation potential will have the same magnitude but opposite sign. For example, the standard oxidation potential of first electrode, Li, Li^+ is + 3.05 V and standard oxidation potential of the last electrode F^-, F_2 is – 2.87 V.

Applications of Electrochemical Series

The main applications of the electrochemical series are given below :

1. Relative strengths of oxidising and reducing agents.

The electrochemical series helps us to pick out substances that are good oxidising agents and those which are good reducing agents. In the electrochemical

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series, the substances are arranged in the decreasing order of reduction potential *i.e.* decreasing tendency for reduction to occur or power as oxidising agent. Therefore, the elements at the top of the table have maximum tendency to get reduced and consequently, they will act as good oxidising agents. On the other hand, the substances at the bottom of the table have lower reduction potential, therefore, they have least tendency to get reduced. Consequently, they may be oxidised and act as good reducing agents. Thus, *the substances which have lower reduction potentials are stronger reducing agents while those which have higher reduction potentials are stronger oxidising agents.* For example, a very high negative reduction potential of lithium electrode indicates that Li^+ cannot accept electrons easily from other species. In other words, lithium can readily lose electrons and, therefore, behaves as strong reducing agent. Thus, **all the substances appearing at the bottom of the series behave as good reducing agents.** For example, Li, K are the best reducing agents.

Similarly, the substances at the top of the table have high reduction potentials and they can be easily reduced and act as oxidising agents. For example, fluorine has the highest electrode potential indicating that fluorine is very powerful oxidizing agent. From the position of the electrodes in the table we can conclude that H^+ is a better oxidising agent than Zn^{2+} but Cu^{2+} is a better oxidising agent than H^+. Thus, **good oxidising agents are the substances appearing at the top of the table.**

2. Comparison of reactivities of metals

The reduction potential values indicate the relative ease with which the various species of metals and ions may be oxidised or reduced. The metals having lower reduction potential, will not be reduced easily. On the contrary, such metals would be easily oxidized to their ions losing electrons. These electrons would reduce the other metals having higher reduction potentials. In other words, a metal having smaller reduction potential can displace metals having larger reduction potentials from the solutions of their salts. For example, copper has lower reduction potential than silver in the electrochemical series, therefore, if copper foils are added to $AgNO_3$ solution, silver is displaced from the solution. In general *a metal occupying lower position in the series can displace the metals lying above it from the solutions of their salts.* In other words, we can say that the metals occupying lower positions in the electrochemical series are more reactive in displacing the other metals from the solutions of their salts.

3. Calculation of the E.M.F. of the cell

The E.M.F. of the cell which is the difference between the reduction potential of the cathode and anode is determined by the following steps :

Step I. Write the two half cell reactions in such a way that the reaction taking place at the left hand electrode is written as an oxidation reaction and that taking place at the right hand electrode is written as reduction.

Step II. Multiply one of the equations if necessary by suitable number to equate the number of electrons in the two equations. However, it may be noted that electrode potential values, E° are not multiplied.

Step III. The E.M.F. of the cell is equal to the difference between the standard electrode potential of the right hand side electrode (E°_R) and the standard electrode potential of the left hand side electrode (E°_L). Thus,

$$E^\circ_{cell} = E^\circ_R - E^\circ_L$$

The electrode potentials of both the electrodes are taken to be reduction potentials.

Step IV. If the E.M.F. of the cell is +ve, the reaction is feasible in the given direction. But if E.M.F. of the cell is –ve, the cell reaction is not feasible in the given direction. The reaction must be occurring in the reverse direction. Thus, to get positive value for the E.M.F. of the cell, the electrodes are to be reversed.

SOLVED EXAMPLES

❑ **Example 38.**

Write the half cell reaction and the overall cell reaction for the electrochemical cell :

$$Zn\,|Zn^{2+}\,(1.0\ M)\,\|\,Pb^{2+}\,(1.0\ M)\,|Pb$$

Calculate the standard e.m.f. for the cell if standard electrode potentials (reduction) for $Pb^{2+}\,|\,Pb$ and $Zn^{2+}\,|\,Zn$ electrodes are – 0.126 V and – 0.763 V respectively.

Solution: Zn electrode acts as anode while Pb electrode acts as cathode and, therefore, oxidation occurs at zinc electrode and reduction occurs at lead electrode. The half cell reactions are :

Oxidation half reaction :

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

Reduction half reaction :

$$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$$

Overall cell reaction :

$$Zn(s) + Pb^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Pb(s)$$

$$\begin{aligned} \text{E.M.F.} &= E^\circ_R - E^\circ_L \\ &= -0.126 - (-0.763) \\ &= \mathbf{0.637\ V.} \end{aligned}$$

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Note. The EMF of the cell can also simply be calculated as :

$$E^\circ_{cell} = E^\circ_R - E^\circ_L$$

If the value of E°_{cell} is positive, then the cell is correctly represented, *i.e.,* oxidation occurs at left electrode (anode) and reduction occurs at the right electrode (cathode). On the other hand, if the value of E°_{cell} comes out to be negative, then the cell is wrongly represented. Its order is reversed to get positive value for E°_{cell}.

4. Predicting feasibility of a redox reaction. The electrochemical series helps in finding out whether a given redox reaction is feasible or not from the E° values of the two electrodes.

In general, a redox reaction is feasible only if the species which has higher reduction potential is reduced *i.e.,* accepts the electrons and the species which has lower reduction potential is oxidised *i.e.,* loses the electrons. Otherwise, a redox reaction is not feasible. In other words, the species to release electrons must have lower reduction potential as compared to the species which is to accept electrons.

The electrochemical series (Table 1) gives the decreasing order of electrode potentials (reduction) of different electrodes on moving down the table. This means that the species to accept the electrons (getting reduced) must be higher in the electrochemical series as compared to the other which is to lose electrons (getting oxidised).

Let us illustrate this by predicting the feasibility of the reaction :

$$Cu^{2+}(aq) + 2Ag(s) \longrightarrow Cu(s) + 2Ag^+(aq)$$

From the electrochemical series (Table 1), E° value of Cu = +0.34 V and the E° value of Ag = + 0.80 V. Since the reduction potential of Ag is more than that of Cu, this means that silver has greater tendency to get reduced in comparison to copper. Thus, the reaction

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

occurs more readily than the reaction

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

Similarly, since reduction potential of copper is less than that of Ag, this means that copper will be oxidised in comparison to Ag. Thus, the reaction,

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

occurs more readily than

$$Ag(s) \longrightarrow Ag^+(aq) + e^-$$

Therefore, silver will be reduced and copper will be oxidised and the above reaction is not **feasible.** Rather the reverse reaction,

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$ can occur.

SOLVED EXAMPLES

❑ **Example 39.**

Iodine (I_2) and bromine (Br_2) are added to a solution containing iodide (I^-) and bromide (Br^-) ions. What reaction would occur if the concentration of each species is 1M ? The electrode potentials for the reactions are :

$$I_2 + 2e^- \longrightarrow 2I^- \qquad E^\circ = +0.54\ V$$
$$Br_2 + 2e^- \longrightarrow 2Br^- \qquad E^\circ = +1.02\ V$$

Solution: Since the reduction potential of Br_2 is more than that of I_2, it means that bromine can readily be reduced. Therefore, I^- will be oxidised to I_2 and this reaction should be written as oxidation. Therefore, the following reactions will occur :

$$Br_2 + 2e^- \longrightarrow 2Br^-$$
$$2I^- \longrightarrow I_2 + 2e^-$$
$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

Alternatively, the problem can also be solved by considering the half cell reactions.

$$(i) \quad I_2 + 2e^- \longrightarrow 2I^- \qquad E^\circ = +0.54\ V$$
$$(ii) \quad Br_2 + 2e^- \longrightarrow 2Br^- \qquad E^\circ = +1.02\ V$$

Since for the feasibility of the reaction, the e.m.f. should be +ve, therefore to get + ve value for the overall cell reaction, subtract the equation representing lower value of E° from the equation representing the higher value of E°. Thus, subtract Eq. (*i*) from (*ii*).

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$
$$E^\circ = 1.02 - 0.54 = \mathbf{0.48\ V}$$

❑ **Example 40.**

What will be the spontaneous reaction between the following half cell reactions?

$$(i) \quad Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s) \qquad E^\circ = -0.74\ V$$
$$(ii) \quad MnO_2(s) + 4H^+ + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l) \qquad E^\circ = 1.28\ V$$

Calculate E°_{cell}.

Solution: Since the reduction potential of reaction (*ii*) is more than that of reaction (*i*) ; reaction (*ii*) will occur as reduction. Therefore, reaction (*i*) should be written as oxidation. To obtain the net reaction, we multiply by appropriate coefficients so that electrons get cancelled.

$$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)] \times 3$$
$$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-] \times 2$$

$$2Cr(s) + 3\,MnO_2(s) + 12H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Mn^{2+}(aq) + 6H_2O$$

$$E^\circ_{cell} = E_{\text{Substance reduced}} - E_{\text{Substance oxidised}}$$
$$= 1.28 - (-0.74) = \mathbf{2.02\ V}$$

❑ **Example 41.**

The standard electrode potential corresponding to the reaction : $Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$ is 1.42 V. Predict (i) if gold can be dissolved in 1M

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HCl solution and (ii) on passing hydrogen gas through gold salt solution, metallic gold will be precipitated or not.

Solution: The standard reduction potential is greater than zero, therefore, reduced form of gold is more stable than hydrogen. In other words, gold cannot be oxidized by hydrogen to give hydrogen. Hence gold does not dissolve in 1 M HCl solution. On the other hand, if hydrogen gas is passed through the salt solution of the gold, it will reduce Au^{3+} ion and metallic gold will be precipitated.

❑ **Example 42.**

Is it possible to store

(i) Copper sulphate in a zinc vessel ?
(ii) Copper sulphate in a silver vessel ?
(iii) Copper sulphate in a nickel vessel ?
(iv) Copper sulphate in a gold vessel ?

Solution: (*i*) From Table 18.1, it is clear that electrode potential of copper ($Cu^{2+} \mid Cu = 0.34$) is more than zinc ($Zn^{2+} \mid Zn = -0.76$ V), therefore, it will be readily reduced to copper and zinc will be oxidized. As a result, zinc vessel will dissolve.

(*ii*) It is possible to store copper sulphate in a silver vessel because silver vessel will not dissolve ($Ag^+ \mid Ag = 0.80$V).

(*iii*) It is not possible to store copper sulphate in nickel vessel because Ni will dissolve ($Ni^{2+} \mid Ni = -0.13$ V).

(*iv*) It is possible to store copper sulphate in gold vessel ($Au^{3+} \mid Au = 1.61$ V).

❑ **Example 43.**

Give two examples each of oxidants which can oxidize

(i) Cl^- (aq) to Cl_2 (g)
(ii) Fe (s) to Fe^{2+} (aq)
(iii) I^- (aq) to I_2 (aq)

Solution:

(*i*) Au, F_2 (*ii*) Ni, Sn
(*iii*) Fe, Ag

5. Predicting whether a metal can liberate hydrogen from the acid or not. The metals like *zinc, magnesium and nickel* can liberate hydrogen from the acids like HCl, H_2SO_4 etc., but metals like copper and silver cannot do so. In general, only those metals can liberate hydrogen from the acids which have negative values of reduction potentials *i.e.*, $-E^\circ$ values. Obviously, hydrogen will have greater tendency to get reduced (accept electrons) and the metal can lose electrons (get oxidised) and hydrogen gas is liberated.

$$\underset{\text{(Monovalent)}}{M} \longrightarrow M^+ (aq) + e^-$$

$$H^+ (aq) + e^- \longrightarrow H \text{ or } \frac{1}{2} H_2$$

Metals like copper and silver have + E° values *i.e.*, electron accepting tendencies. Their atoms are not in a position to lose electrons to H^+ ions of the acid. Therefore, hydrogen gas is not liberated.

Practice Problems

◑ **21.** Calculate E° For the cell :

$Al \mid Al^{3+} (1M) \parallel Cu^{2+} (1\ M) \mid Cu$

Given $E^\circ (Al^{3+} \mid Al) = -1.66$ V and

$E^\circ (Cu^{2+} \mid Cu) = 0.34$ V

◑ **22.** The standard electrode potentials of some electrodes are :

Electrode	$Zn^{2+} \mid Zn$	$Cd^{2+} \mid Cd$	$Ag^+ \mid Ag$	$Fe^{2+} \mid Fe$
E° (V)	–0.76	–0.40	0.80 V	–0.44 V

Which of the following cells are feasible and give their E°_{cell}?

(*i*) $Zn \mid Zn^{2+} \parallel Cd^{2+} \mid Cd$ (*ii*) $Fe \mid Fe^{2+} \parallel Zn^{2+} \mid Zn$
(*iii*) $Cd \mid Cd^{2+} \parallel Ag^+ \mid Ag$ (*iv*) $Fe \mid Fe^{2+} \parallel Ag^+ \mid Ag$

◑ **23.** An iron wire is immersed in a solution containing $ZnSO_4$ and $NiSO_4$. When the concentration of each salt is 1 M, predict giving reasons which of the following reactions is likely to proceed ?

(*i*) Iron reduces Zn^{2+} ions
(*ii*) Iron reduces Ni^{2+} ions. Given
$E^\circ (Zn^{2+} \mid Zn) = -0.76$V, $E^\circ (Fe^{2+} \mid Fe) = -0.44$V,
and $E^\circ (Ni^{2+} \mid Ni) = -0.25$V

◑ **24.** Can a solution of 1 M $CuSO_4$ be stored in a vessel made of nickel metal ? Given $E^\circ (Ni^{2+} \mid Ni) = -0.25$V and $E^\circ (Cu^{2+} \mid Cu) = 0.34$V

◑ **25.** Can chlorine gas be stored in a copper cylinder? Given $E^\circ (Cu^{2+} \mid Cu) = 0.34$V and $E^\circ (Cl^- \mid Cl) = 1.36$V.

◑ **26.** Why does blue colour of copper sulphate get discharged when zinc rod is dipped in it ?

Given $E^\circ (Cu^{2+} \mid Cu) = 0.34$V and $E^\circ (Zn^{2+} \mid Zn) = -0.76$V.

◑ **27.** A copper wire is dipped in silver nitrate solution in beaker A and a silver wire is dipped in a solution of copper sulphate kept in beaker B. If the standard electrode potential for

$Cu^+ + 2e^- \longrightarrow Cu$ is +0.34 and for

$Ag^+ + e^- \longrightarrow Ag$ is + 0.80 V.

Given $E^\circ (Ni^{2+} \mid Ni) = -0.25$V and $E^\circ (Cu^{2+} \mid Cu) = 0.34$V

Predict in which beaker the ions present will get reduced ?

Answers to Practice Problems

◐ **21.** 2.0 V
◐ **22.** (*i*) Feasible, + 0.36 V (*ii*) not feasible, –0.32 V
(*iii*) feasible, +1.20 V (*iv*) feasible, +1.24 V.
◐ **23.** Iron reduces Ni^{2+} ions.
◐ **24.** No.
◐ **25.** No.
◐ **27.** In beaker A, Ag^+ will be reduced.

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Conceptual Questions

CONCEPTUAL QA

Q. 1. Arrange the following molecules in the decreasing order of oxidation state (+ve to –ve) of nitrogen : NO_2, NH_3, HN_3, NO_2^-, N_2H_4.

Ans. Oxidation states of N are :

NO_2 = + 4, NH_3 = –3, $HN_3 = -\frac{1}{3}$

NO_2^- = + 3, N_2H_4 = –2

Decreasing order of oxidation state :

$NO_2 > NO_2^- > HN_3 > N_2H_4 > NH_3$

Q. 2. Can the reaction :

$Cr_2O_7^{2-} + H_2O \longrightarrow 2CrO_4^{2-} + 2H^+$

be regarded as a redox reaction ?

Ans. In this reaction,

Oxidation number of Cr in $Cr_2O_7^{2-}$ = +6

Oxidation number of Cr in CrO_4^{2-} = +6

Since during this reaction, the oxidation number of Cr has neither increased nor decreased, therefore, the above reaction cannot be regarded as a redox reaction.

Q. 3. Calculate the oxidation number of Fe in

(*i*) Fe_3O_4 (*ii*) $Fe_4[Fe(CN)_6]_3$

Ans. (*i*) Fe_3O_4 $3x - 8 = 0$ or $x = 8/3$ (fractional)

Actually the composition of Fe_3O_4 is $FeO.Fe_2O_3$

The O.N. of Fe in FeO is +2 and in Fe_2O_3, it is +3.

On the average O.N. comes out to be 8/3.

(*ii*) $Fe_4[Fe(CN)_6]_3$. In this case the O.N. of Fe in the bracket is +2 and that of Fe outside the brackets is +3.

$Fe_4^{+3}[Fe^{+2}(CN)_6]_3$

Q. 4. Split the following redox reactions in the oxidation and reduction half reactions :

(*i*) $2K\,(s) + Cl_2\,(g) \longrightarrow 2KCl\,(s)$

(*ii*) $2Al\,(s) + 3Cu^{2+}\,(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu\,(s)$

Ans. (*i*) Oxidation half reaction : $2K\,(s) \longrightarrow 2K^+(aq) + 2e^-$

Reduction half reaction : $Cl_2\,(g) + 2e^- \longrightarrow 2Cl^-$

(*ii*) Oxidation half raction : $2Al\,(s) \longrightarrow 2Al^{3+}\,(aq) + 6e^-$

Reduction half reaction : $3Cu^{2+} + 6e^- \longrightarrow 3Cu\,(s)$

Q. 5. Nitric acid acts only as an oxidising agent while nitrous acid acts both as an oxidising as well as reducing agent. Explain.

Ans. (*i*) HNO_3. Oxidation number of N in HNO_3 is +5.

Maximum oxidation number of N is +5 because it has five electrons in the valence shell ($2s^2 2p^3$).

Minimum oxidation number of N is –3 because it can accept 3 more electrons to get noble gas configuration.

Since O.N. of N in HNO_3 is maximum, therefore, it can only decrease. Thus, **HNO_3 can act as an oxidising agent**.

(*ii*) HNO_2. Oxidation number of N = + 3

Maximum O.N. of N = + 5

Minimum O.N. of N = – 3

Therefore, the O.N. of N can increase by losing electrons or can decrease by accepting electrons. Thus, HNO_2 can act both as an oxidising as well as a reducing agent.

Q. 6. Calculate the oxidation number of the underlined element in

(*a*) $\underline{V}O_2^+$ (*b*) $\underline{U}O_2^{2+}$ (*c*) $Ba_2\underline{Xe}O_6$ (*d*) $K_4\underline{P}_2O_7$ (*e*) $K_2\underline{S}$

Ans. The O.N. of underlined atom is represented by x

(*a*) $\underline{V}O_2^+$ $x + 2(-2) = +1$ or $x = +5$

(*b*) $\underline{U}O_2^{2+}$ $x + 2(-2) = +2$ or $x = +6$

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(*c*) $Ba_2\underline{Xe}O_6$ $+2(2) + x + 6(-2) = 0$ or $x = +8$

(*d*) $K_4\underline{P_2}O_7$ $1\times 4 + 2x + 7(-2) = 0$ or $x = +5$

(*e*) $K_2\underline{S}$ $1\times 2 + x = 0$ or $x = -2$

Q. 7. Which of the following equations represent oxidation reduction reaction ? Identify each oxidising agent and each reducing agent.

(*a*) $KOH + H_2O_2 \longrightarrow KHO_2 + H_2O$

(*b*) $Cr_2O_7^{2-} + 2\ OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

(*c*) $K + O_2 \longrightarrow KO_2$

(*d*) $Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$

Ans.(*i*) *a*, *b*, and *d* are not redox reactions.

c is a redox reaction. The oxidising agent is O_2 and reducing agent is K.

Q. 8. Identify the oxidising and reducing agent in the following reaction :

$Fe^{2+} + 2H^+ + NO_3^- \longrightarrow Fe^{3+} + NO_2 + H_2O$

Ans. $\overset{+2}{Fe^{2+}} + 2H^+ + \overset{+5}{NO_3^-} \longrightarrow \overset{3+}{Fe^{3+}} + \overset{+4}{NO_2} + H_2O$

Fe^{2+} is oxidised to Fe^{3+} by NO_3^- ion and therefore, NO_3^- is an oxidising agent. NO_3^- is reduced from N(+5) to N(+4) in NO_2 by Fe^{2+} and therefore, Fe^{2+} is a reducing agent.

CONCEPTUAL QA

Q. 9. Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2. Explain Why ?

Ans. PbO is a basic oxide and reacts with. HNO_3 and simple acid base reaction takes place.

$2PbO + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O$

But in PbO_2, lead is in +4 oxidation state and cannot be further oxidised. Therefore, it does not react with HNO_3.

Q. 10. Predict the maximum and minimum oxidation states for (*i*) Cl (*ii*) Ti

Ans. Maximum oxidation state for Cl = +7

Minimum oxidation state for Cl = –1

Maximum oxidation state for Ti = +4

Minimum oxidation state for Ti = 0

For metals minimum O.N. is zero but for non–metals, it is group number minus 8.

Q. 11. The electrode reduction potentials of four metallic elements A, B, C and D are respectively +0.79, – 0.74, 1.08 and – 0.31 V. Arrange these in order of decreasing electropositive character.

Ans. Higher the electrode reduction potential, lower is its tendency to lose electrons and therefore, lower is the electropositive character of the metal. So, the metals can be arranged as : B, D, A, C

Q. 12. An iron rod is immersed in a solution containing $NiSO_4$ and $ZnSO_4$. When the concentration of each salt is 1M, predict giving reasons which of the following reactions is likely to proceed ?

(*i*) Iron reduces Zn^{2+} ions (*ii*) Iron reduces Ni^{2+} ions

Given : $E^\circ_{(Zn^{2+}|Zn)} = -0.76$ V, $E^\circ_{(Fe^{2+}|Fe)} = -0.44$ V and $E^\circ_{(Ni^{2+}|Ni)} = -0.25$ V

Ans. (*i*) The reduction potential of iron is more than that of zinc. Therefore, iron will be reduced. In other words, Zn^{2+} will not be reduced by iron.

(*ii*) The reduction potential of Ni^{2+} is more than that of iron. Therefore, Ni^{2+} will be reduced by iron.

Q. 13. Which of the following reactions are not feasible ?

(*a*) $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

(*b*) $I_2(s) + 2Br^-(aq) \longrightarrow 2I^-(aq) + Br_2$

(*c*) $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2Fe^{2+}(aq)$

(*d*) $2Ag + 2H^+(aq) \longrightarrow H_2 + 2Ag^+(aq)$

Ans. (*a*) and (*c*) are feasible.

Q. 14. At what concentration of Cu^{2+} (*aq*) will its electrode potential become equal to its standard electrode potential ?

Ans. At 1 M concentration.

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Q.15. How does Cu_2O act as both oxidant and reductant ? Explain with proper reactions showing the change of oxidation number in each case.

Ans. In Cu_2O, copper is in +1 (Cu^+) oxidation state and it undergoes disproportionation to form Cu and Cu^{2+} as :

$$2Cu^+(aq) \longrightarrow Cu(s) + Cu^{2+}(aq)$$

Thus, Cu^+ or Cu_2O acts both as an oxidant as well as a reductant.

For example,

(*i*) When heated in air, Cu_2O is oxidised to CuO

$$\overset{+1}{Cu_2O} + \frac{1}{2}O_2 \longrightarrow \overset{+2}{2CuO}$$

Thus, Cu_2O acts as a reductant and reduces O_2 to O^{2-}.

(*ii*) When heated with Cu_2S, it oxidises S^{2-} to SO_2 and hence Cu_2O acts as an oxidant.

$$\overset{+1}{2Cu_2O} + \overset{+1}{Cu_2S} \longrightarrow \overset{0}{6Cu} + SO_2$$

Q. 16. A solution of silver nitrate was stirrred with an iron rod. Will it cause any change in the concentration of silver and nitrate ions ?

Ans. The E^o of $Fe^{2+} \mid Fe$ (– 0.44 V) is lower than that of $Ag^+ \mid Ag$ (+0.80 V), therefore, Ag^+ gets reduced and Fe gets oxidised. As a result, the concentration of Ag^+ ions decreases and that of NO_3^- ions remains unchanged.

$$2\,Ag^+(aq) + 2\,NO_3^-(aq) + Fe(s) \longrightarrow 2\,Ag(s) + Fe^{2+}(aq) + 2\,NO_3^-(aq)$$

Q. 17. What is the oxidation number of N in HNO_4?

Ans. By conventional method, O.N. of N is : $+1 + x + 4(-2) = 0$ or $x = +7$.

However, N cannot have O.N. more than +5. Therefore, O.N. of N in HNO_4 (peroxynitric acid) must be calculated from its structure. The structure of HNO_4 is $H—O—O—\underset{\underset{O}{\|}}{N}\longrightarrow O$. It contains one peroxide linkage and therefore, each of the two oxygen atoms of peroxide bonds has an O.N. of –1.

Thus, $+1 - 1 - 1 + x - 2 - 2 = 0$ or $x = +5$.

Q. 18. Calculate the oxidation number of nickel in $Ni(CO)_4$, iron in $Fe(CO)_5$ and carbon in CH_2O.

Ans. $Ni(CO)_4 : x + 4(0) = 0$ or $x = 0$

$Fe(CO)_5 : x + 5(0) = 0$ or $x = 5$

$CH_2O : x + 2(+1) - 2 = 0$ or $x = 0$.

Q. 19. At what concentration of Zn^{2+} (aq) will its electrode potential become equal to its standard electrode potential ?

Ans. At 1 M concentration.

Q. 20. The E^o ($Al^{3+} \mid Al$) and E^o ($Cu^{2+} \mid Cu$) are – 1.66 V and + 0.34 V respectively. Is the cell : $Cu \mid Cu^{2+}$ (1M) $\| Al^{3+}$ (1M) $\mid Al$ feasible or not feasible?

Ans. Not feasible.

Chapter Summary

Key Terms

- **Oxidation** is a process which involves loss of electrons or increase in oxidation number.
- **Reduction** is a process which involves gain of electrons or decrease in oxidation number.
- **Oxidation number** is the charge which an atom appears to have when all other atoms are removed from it as ions.
- **Oxidising agent** is a substance which accepts one or more electrons or its oxidation number decreases.
- **Reducing agent** is a substance which loses one or more electrons or its oxidation number increases.

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QUICK CHAPTER ROUND UP

Oxidation & Reduction

Electronic concept

- **Oxidation :** a process in which one or more electrons are lost.
- **Reduction :** a process in which one or more electrons are gained.
- **Oxidising agent** or **oxidant :** a substance which can accept one or more electrons.
- **Reducing agent** or **reductant :** a substance which can give one or more electrons.

In terms of oxidation number

- **Oxidation:** a process which involves increase in oxidation number.
- **Reduction:** a process which involves decrease in oxidation number.
- **Oxidising agent:** a substance whose oxidation number decreases.
- **Reducing agent:** a substance whose oxidation number increases.

➢ Oxidation and reduction always occur side by side.

Oxidation number

- for elementary state, O.N is zero.
  e.g., He(O.N. = 0), H_2 (O.N.=0), S_8(O.N.=0)
- oxidation number of hydrogen is +1 except in hydrides NaH, LiH, CaH_2 (−1).
- Oxidation number of oxygen is always −2 except
  in peroxides, H_2O_2, Na_2O_2 (−1)
  in superoxides KO_2 (−1/2)
  in OF_2 (+2)
  O_2F_2 (+1)

- Combination reaction

$$2Mg + O_2 \longrightarrow 2MgO$$

- Decomposition reaction

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

- Displacement reaction

$$CuSO_4 + Zn \longrightarrow Cu + ZnSO_4$$

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

- **Disproportionation reactions**
  The reactions in which the oxidation number of an element both increases and decreases.
  e.g., $2H_2O_2 \longrightarrow 2H_2O + O_2$
  In this case the oxidation number of O decreases from −1 to −2 (in H_2O) and increases from −1 to 0 (in O_2).
  - $Cl_2 + 2OH^- \longrightarrow OCl^- + Cl^- + H_2O$
    O.N. of Cl increases from 0 to +1 (in OCl^-) and decreases from 0 to −1 (in Cl^-).
  - $3ClO^- \longrightarrow ClO_3^- + 2Cl^-$ is also a disproportionation reaction because O.N. of Cl increases from +1 (in ClO^-) to +5 (in ClO_3^-) and decreases from +1 to −1 (in Cl^-).

Oxidation and **reduction** reactions can be blalanced by **oxidation number method** and **half reaction method.**

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NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. Assign oxidation number to the underlined elements in each of the following species :

(a) $\underline{NaH_2}PO_4$ **(b)** $\underline{NaH}SO_4$

(c) $H_4\underline{P_2}O_7$ **(d)** $K_2\underline{Mn}O_4$

(e) $\underline{Ca}O_2$ **(f)** $\underline{NaB}H_4$

(g) $H_2\underline{S_2}O_7$ **(h)** $\underline{KAl}(SO_4)_2.12H_2O$

Ans. Let the oxidation number of underlined atom be x.

(a) $\overset{+1}{Na}\ \overset{+1}{H_2}\ \overset{x}{P}\ \overset{-2}{O_4}$

$1(+1) + 2(+1) + x + 4(-2) = 0 \quad \therefore x = +5$

Oxidation number of P in NaH_2PO_4 is **+ 5**

(b) $\overset{+1}{Na}\ \overset{+1}{H}\ \overset{x}{S}\ \overset{-2}{O_4}$

$1(+1) + 1(+1) + x + 4(-2) = 0$

$x - 6 = 0 \quad \therefore \quad x = +6$

(c) $\overset{+1}{H_4}\ \overset{x}{P_2}\ \overset{-2}{O_7}$

$4(+1) + 2(x) + 7(-2) = 0$

$2x - 10 = 0 \quad \therefore \quad x = +5$

(d) $\overset{+1}{K_2}\ \overset{x}{Mn}\ \overset{-2}{O_4}$

$2(+1) + x + 4(-2) = 0$

$x - 6 = 0 \quad \therefore \quad x = +6$

(e) $\overset{+2}{Ca}\ \overset{x}{O_2}$

$+2 + 2(x) = 0 \quad \therefore \quad x = -1$

(f) $\overset{+1}{Na}\ \overset{x}{B}\ \overset{-1}{H_4}$

$1(+1) + x + 4(-1) = 0$

$x - 3 = 0 \quad \therefore \quad x = +3$

(g) $\overset{+1}{H_2}\ \overset{x}{S_2}\ \overset{-2}{O_7}$

$2(+1) + 2(x) + 7(-2) = 0$

$2x - 12 = 0 \quad \therefore \quad x = +6$

(h) $\overset{+1}{K}\ \overset{+3}{Al}\ (S\ \overset{x}{O_4})_2 . 12\overset{+1}{H_2}\ \overset{-2}{O}$

$1(+1) + 1(+3) + 2x + 8(-2) + 12(2 \times 1 - 2) = 0$

$2x - 12 = 0 \quad \therefore \quad x = +6$

Q. 2. What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results ?

(a) $\underline{KI_3}$ **(b)** $H_2\underline{S_4}O_6$

(c) $\underline{Fe_3}O_4$ **(d)** $\underline{CH_3}\underline{CH_2}OH$

(e) $\underline{CH_3}\underline{COOH}$

Ans. (a) In KI_3, since the oxidation number of K is +1, therefore, the average oxidation number of iodine is $-\frac{1}{3}$.

$\overset{+1}{K}\ \overset{x}{I_3} \qquad +1 + 3(x) = 0 \qquad \therefore \quad x = -\frac{1}{3}$

But oxidation number cannot be fractional. In fact KI_3 exists as : $K^+\ [I\text{–}I \longleftarrow I]^-$ in which a coordinate bond is formed between I_2 molecule and I^-. In this the oxidation number of two iodine atoms forming I_2 molecule is zero and that of iodine forming the coordinate bond is –1. Thus, the actual oxidation number of atoms are :

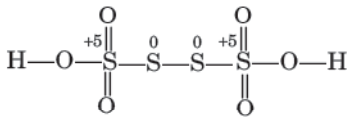
$\overset{+}{K}\ \overset{0}{I_2}\ \overset{-1}{I}$

(b) **$H_2S_4O_6$.** The oxidation number may be calculated as :

$\overset{+1}{H_2}\ \overset{x}{S_4}\ \overset{-2}{O_6}$

$2(+1) + 4x + 6(-2) = 0 \quad \therefore \quad x = +\frac{5}{2}$

Since oxidation number cannot be fractional, the actual oxidation number of different S atoms are:



(c) **Fe_3O_4.** The oxidation number may be calculated as :

$\overset{x}{Fe_3}\ \overset{-2}{O_4}$

$3x + 4(-2) = 0 \quad$ or $\quad \therefore \quad x = +\frac{8}{3}$

In fact, Fe_3O_4 exists as a mixture of FeO and Fe_2O_3 as :

$\overset{+2}{FeO}.\ \overset{+3}{Fe_2}\ \overset{-2}{O_3}$

Fe has oxidation number of +2 and +3.

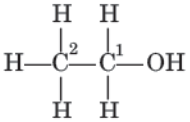
(d) CH_3CH_2OH – By conventional method, the oxidation number may be calculated as :

$\overset{x}{C}\ \overset{+1}{H_3}\ \overset{x}{C}\ \overset{+1}{H_2}\ \overset{-2}{O}\ \overset{+1}{H}$

$x + 3(+1) + x + 2(+1) + 1(-2) + 1(+1) = 0$

$2x + 4 = 0 \quad \therefore \quad x = -2$

In fact, ethanol may be written as :



C_2 is attached to three H atoms (less electronegative than carbon) and one CH_2OH group (more electronegative than carbon). Therefore,

O.N. of C_2 : $3(+1) + x + 1(-1) = 0$ or $x = -2$

C_1 is attached to one OH (O.N. = –1) and one CH_3(O.N. = +1) and two H-atoms

O.N. of $C_1 = +1 + 2(+1) + x + 1(-1) = 0 \quad \therefore x = -2$

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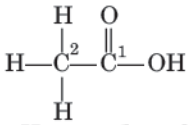
(*e*) CH_3COOH. By conventional method

$$\overset{x}{C}\ \overset{+1}{H_3}\quad \overset{x}{C}\ \overset{-2}{O}\ \overset{-2}{O}\ \overset{+1}{H}$$

$x + 3(+1) + x + (-2) + (-2) + 1(+1) = 0$

$2x + 0 = 0 \qquad \therefore\ x = \mathbf{0}$

But according to structure,



C_2 is attached to three H atoms (less electronegative than C) and one –COOH group (more electronegative than C).

O.N. of $C_2 = 3(+1) + x + 1(-1) = 0 \quad \therefore\ x = -2$

C_1 is attached to one oxygen atom by a double bond, one OH-group (O.N. = –1) and one CH_3 (O.N. = +1).

O.N. of $C_1 = +1 + x + 1(-2) + 1(-1) = 0$

$x - 2 = 0$ or $x = +2$

Q.3. Justify that the following reactions are redox reactions:

(*a*) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$

(*b*) $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

(*c*) $4BCl_3(g) + 3LiAlH_4(s) \longrightarrow 2B_2H_6(g) + 3LiCl(s) + 3AlCl_3(s)$

(*d*) $2K(s) + F_2(g) \longrightarrow 2K^+F^-(s)$

(*e*) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

Ans. (*a*) $\overset{+2\ -2}{Cu}O(s) + \overset{0}{H_2}(g) \longrightarrow \overset{0}{Cu}(s) + \overset{+1\ -2}{H_2}O(g)$

In this case, O.N. of Cu decreases from +2 (in CuO) to 0 (in Cu) and that of H increase from 0 (in H_2) to +1 (in H_2O). Therefore, CuO is reduced to Cu while H_2 is oxidised to H_2O. Thus, this is a redox reaction.

(*b*) $\overset{+3\ -2}{Fe_2}O_3 + 3\overset{+2\ -2}{C}O \longrightarrow 2\overset{0}{Fe}(s) + 3\overset{+4\ -2}{C}O_2$

O.N. of Fe decreases from +3 (in Fe_2O_3) to 0 (in Fe) and that of C increases from +2 (in CO) to +4 (in CO_2). Therefore, Fe_2O_3 is reduced while CO is oxidised. Thus, this is a redox reaction.

(*c*) $4\overset{+3\ -1}{B}Cl_3(s) + 3\overset{+1\ +3\ -1}{LiAlH_4}(s) \longrightarrow \overset{-3\ +1}{2B_2H_6}(g) + 3\overset{+1\ -1}{LiCl}(s) + 3\overset{+3\ -1}{AlCl_3}(s)$

O.N. of B. decreases from +3 (in BCl_3) to –3 in B_2H_6 and that of H increases from –1 (in $LiAlH_4$) to + 1 (in B_2H_6). Therefore, BCl_3 is reduced and $LiAlH_4$ is oxidised. Hence, it is a redox reaction.

(*d*) $2\overset{0}{K}(s) + \overset{0}{F_2}(g) \longrightarrow 2\overset{+1}{K^+} + \overset{-1}{F^-}(s)$

O.N. of K increases from 0 (in K) to +1 (in K^+) and that of F decreases from 0 in (F_2) to – 1 (in F^-). Hence, K has been oxidised while F_2 has been reduced. Therefore, it is a redox reaction.

(*e*) $\overset{-3\ +1}{4NH_3}(g) + 5\overset{0}{O_2}(g) \longrightarrow 4\overset{+2\ -2}{NO}(g) + 6\overset{+1\ -2}{H_2O}(g)$

In this case O.N. of N increases from – 3 (in NH_3) to +2 (in NO) and that of O decreases from 0 (in O_2) to – 2 (in H_2O). Therefore, NH_3 has been oxidised while O_2 has been reduced. Hence, it is a redox reaction.

Q. 4. Fluorine reacts with ice and results in the change:

$H_2O(s) + F_2(g) \longrightarrow HF(g) + HOF(g)$

Justify that this reaction is a redox reaction.

Ans. $\overset{+1\ -2}{H_2O}(s) + \overset{0}{F_2}(g) \longrightarrow \overset{+1\ -1}{HF} + \overset{+1\ -2\ +1}{HOF}$

In this case, F_2 is reduced to HF and oxidised to HOF. Therefore, it is redox reaction. HOF is unstable and decomposes to form O_2 and HF.

$$2\overset{+1\ -2\ +1}{HOF} \longrightarrow 2\overset{+1\ -1}{HF} + \overset{0}{O}$$

In this reaction, F of HOF is reduced while O of HOF is oxidised. Therefore, it is a redox reaction but not a disproportionation reaction. If oxygen of HOF disproportionates, then oxygen must show three oxidation states. If we assume that oxidation state of O is zero in HOF, then its oxidation state decreases to –2. HOF is reduced to H_2O and increases to +2 if if HOF gets oxidised to OF_2.

Therefore, the possible reaction is

$$2\overset{+1\ 0\ -1}{HOF} \longrightarrow \overset{+1\ -2}{H_2O} + \overset{+2\ -1}{OF_2}$$

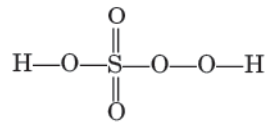
Q.5. Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, $Cr_2O_7^{2-}$ and NO_3^-. Suggest structure of these compounds. Count for the fallacy.

Ans. (*i*) **H_2SO_5.** By conventional method

$$\overset{+1}{H_2}\ \overset{x}{S}\ \overset{-2}{O_5}$$

$2(+1) + x + 5(-2) = 0 \qquad$ or $\qquad x = \mathbf{+8}$

This is not possible because S cannot have O.N. more than 6. The fallacy is overcomed if we calculate its O.N. from its structure as :



$\underset{\text{(for H)}}{2\times(+1)} + \underset{\text{(for S)}}{x} + \underset{\text{(for O—O)}}{2(-1)} + \underset{\text{(for other O atom)}}{3\times(-2)} = 0$

or $\boldsymbol{x = +6}$

(*ii*) **$Cr_2O_7^{2-}$**

$2x + 7(-2) = -2$

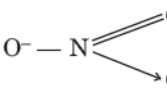
$2x = 12 \qquad \therefore\ x = \mathbf{+6}$

This is correct and there is no fallacy.

(*iii*) **NO_3^-.** By conventional method,

$x + 3(-2) = -1 \qquad$ or $\qquad x = +5$

From the structure,



$\underset{\text{(for O}^-\text{)}}{x} + \underset{\text{(for = O)}}{1(-1)} + \underset{\text{(for }\rightarrow\text{O)}}{1(-2)} = 0 \quad$ or $\quad x = +5$

Hence, there is no fallacy about O.N. of N in NO_3^- as + 5 whether we calculate by conventional method or by chemical bonding.

Q.6. Write formulas for the following compounds:

(*a*) Mercury (II) chloride

(*b*) Nickel (II) sulphate

(*c*) Tin (IV) oxide

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(d) Thallium (I) sulphate
(e) Iron (III) sulphate
(f) Chromium (III) oxide

Ans. (a) $HgCl_2$ (b) $NiSO_4$ (c) SnO_2
(d) Tl_2SO_4 (e) $Fe_2(SO_4)_3$ (f) Cr_2O_3

Q. 7. Suggest a list of the substances where carbon can exhibit oxidation states from – 4 to + 4 and nitrogen from – 3 to + 5.

Ans. *Refer Solved Example 8. (Page 11).*

Q. 8. While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why ?

Ans. *Refer HOTS Questions, Q.1 (Page 58).*

Q. 9. Consider the reactions :

(a) $6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

(b) $O_3(g) + H_2O_2(l) \longrightarrow H_2O(l) + 2O_2(g)$

Why it is more appropriate to write these reactions as :

(a) $6CO_2 + 12H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$

(b) $O_3(g) + H_2O_2(l) \longrightarrow H_2O(l) + O_2(g) + O_2(g)$

Also suggest a technique to investigate the path of the above (a) and (b) redox reactions.

Ans. It is believed that the photosynthesis reaction occurs in two steps. In the first step, H_2O decomposes to give H_2 and O_2 in the presence of chlorophyll and the H_2 produced reduces CO_2 to $C_6H_{12}O_6$ in the second step. During the second step, some H_2O molecules are also produced and therefore, the reaction occurs as :

(*i*) $12H_2O\,(l) \longrightarrow 12H_2(g) + 6O_2\,(g)$

(*ii*) $6CO_2(g) + 12H_2(g) \longrightarrow C_6H_{12}O_6\,(s) + 6H_2O(l)$

(*iii*) $6CO_2(g) + 12H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6H_2O(l) + 6O_2(g)$

Therefore, it is more appropriate to write the reaction for photosynthesis as (iii) because it means that 12 molecules of H_2O are used per molecule of carbohydrate and $6H_2O$ molecules are produced per molecule of carbohydrate during the process.

(ii) O_2 is written two times in the product which suggests that O_2 is being obtained from the two reactants as:

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$
$$H_2O_2\,(l) + O\,(g) \longrightarrow H_2O\,(l) + O_2(g)$$
$$O_3(g) + H_2O_2\,(l) \longrightarrow H_2O(l) + O_2(g) + O_2(g)$$

The path of the reaction can be studied by using H_2O^{18} in reaction (a) or by using $H_2O_2{}^{18}$ or $O_3{}^{18}$ in reaction (*b*).

Q. 10. The compound AgF_2 is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why ?

Ans. In AgF_2, oxidation state of Ag is +2 which is very unstable. Therefore, it readily accepts an electron to form a more stable oxidation state of +1 as

$$Ag^{2+} + e^- \longrightarrow Ag^+$$

Therefore, AgF_2 if formed will act as a strong oxidising agent.

Q. 11. Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations.

Ans. (*i*) C is a reducing agent while O_2 is an oxidising agent. If excess of C is burnt in a limited supply of O_2, CO is formed in which the oxidation state of C is +2. However, if O_2 is excess, the initially formed CO gets oxidised to CO in which the oxidation state of C is +4.

$$\underset{\text{(excess)}}{2C(s)} + O_2(g) \longrightarrow \overset{+2}{2CO}$$

$$C(s) + \underset{\text{(excess)}}{O_2(g)} \longrightarrow \overset{+4}{CO_2}$$

(*ii*) Sodium is a reducing agent while O_2 is an oxidising agent. When excess of Na is used, sodium oxide is formed in which the oxidation state of O is –2. If however, excess of O_2 is used, Na_2O_2 is formed in which the oxidation state of O is –1, which is higher than –2.

$$\underset{\text{(excess)}}{4Na(s)} + O_2(g) \longrightarrow 2\overset{-2}{Na_2O}(s)$$

$$2Na(s) + \underset{\text{(excess)}}{O_2(g)} \longrightarrow \overset{-1}{Na_2O_2}(s)$$

(*iii*) P_4 is a reducing agent while Cl_2 is an oxidising agent. When excess of P_4 is used, PCl_3 is formed in which the oxidation state of P is +3. However, if excess of Cl_2 is used, then initially formed PCl_3 reacts further to form PCl_5, in which the oxidation state of P is +5.

$$\underset{\text{(excess)}}{P_4(s)} + 6Cl_2 \longrightarrow \overset{+3}{4PCl_3}$$

$$P_4(s) + \underset{\text{(excess)}}{10Cl_2} \longrightarrow \overset{+5}{4PCl_5}$$

Q. 12. How do you account for the following observations ?

(a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why ? Write a balanced redox equation for the reaction.

(b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapour of bromine. Why ?

Ans. When conc. H_2SO_4 is added to an inorganic mixture containing chloride, a pungent smelling gas HCl is produced because a stronger acid displaces a weaker acid from its salt.

$$2NaCl + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HCl$$
$$2\,HCl + H_2SO_4 \not\longrightarrow Cl_2 + SO_2 + 2H_2O$$

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Since HCl is a weak reducing agent, it cannot reduce H_2SO_4 to SO_2 and therefore, HCl is not oxidised to chlorine.

However, if the mixture contains bromide ion, the initially produced HBr is a stronger reducing agent. Therefore, it reduces H_2SO_4 to SO_2 and itself gets oxidised to produce red vapour of Br_2.

$$2\ NaBr + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HBr$$
$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

Q. 13. Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions :

(a) $2AgBr(s) + C_6H_6O_2(aq) \longrightarrow 2Ag(s) + 2HBr(aq) + C_6H_4O_2(aq)$

(b) $HCHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \longrightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2H_2O(l)$

(c) $HCHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \longrightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O(l)$

(d) $N_2H_4(l) + 2H_2O_2(l) \longrightarrow N_2(g) + 4H_2O(l)$

(e) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

Ans.

Reduction

$\overset{+1}{2AgBr(s)} + C_6H_6O_2(aq) \longrightarrow 2Ag(s) + 2HBr(aq) + \overset{0}{C_6H_4O_2(aq)}$

Oxidation

AgBr : reduced, $C_6H_6O_2$ (aq) : oxidised

AgBr : Oxidising agent, $C_6H_6O_2$ (aq) : reducing agent

Reduction

(b) $HCHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^- \longrightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2H_2O(l)$

Oxidation

$[Ag(NH_3)_2]^+$ (aq) : reduced, $HCHO(l)$: oxidised

$[Ag(NH_3)_2]^+$ (aq) : oxidising agent, $HCHO(l)$: reducing agent

Reduction

(c) $HCHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O$

Oxidation

Cu^{2+} (aq) : reduced, $HCHO(l)$: oxidised

Cu^{2+} (aq) : oxidising agent, $HCHO(l)$: reducing agent

Reduction

(d) $N_2H_4(l) + 2H_2O_2(l) \longrightarrow N_2(g) + 4H_2O(l)$

Oxidation

H_2O_2 : reduced, $N_2H_4(l)$: oxidised

H_2O_2 : oxidising agent, $N_2H_4(l)$: reducing agent

Reduction

(e) $\overset{0}{Pb(s)} + \overset{+4}{PbO_2(s)} + 2H_2SO_4(aq) \longrightarrow \overset{+2}{2PbSO_4(s)} + 2H_2O(l)$

Oxidation

PbO_2 : reduced, $Pb(s)$: oxidised

PbO_2 (s) : oxidising agent, $Pb(s)$: reducing agent

Q. 14. Consider the reactions :

$$2S_2O_3^{2-}(aq) + I_2(s) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$
$$S_2O_3^{2-}(aq) + 2Br_2(l) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$$

Why does the same reductant, thiosulphate react differently with iodine and bromine ?

Ans. The O.N. of S in $S_2O_3^{2-}$ is +2, in $S_4O_6^{2-}$ it is +2.5 (average) and in SO_4^{2-} it is +6. Since Br_2 is a stronger oxidising agent than I_2, it oxidises S of $S_2O_3^{2-}$ to SO_4^{2-} (with higher O.N. of +6). However, I_2 being a weaker oxidising agent oxidises S of $S_2O_3^{2-}$ into a lower O.S. of +2.5 in $S_4O_6^{2-}$. Therefore, $S_2O_3^{2-}$ reacts differently with Br_2 and I_2.

Q. 15. Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

Ans. The oxidising power of halogens decreases in the order : $F_2 > Cl_2 > Br_2 > I_2$. Therefore, F_2 can oxidise Cl^-, Br^- and I^- to respective Cl_2, Br_2, I_2.

$$F_2(g) + 2Cl^-(aq) \longrightarrow 2F^-(aq) + Cl_2(g)$$
$$F_2(g) + 2Br^-(aq) \longrightarrow 2F^-(aq) + Br_2(l)$$
$$F_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(s)$$

Cl_2 can oxidise Br^- to Br_2 and I^- to I_2

$$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$$
$$2Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(s)$$

However, Cl_2 cannot oxidise F^- to F_2.

Br_2 can oxidise only I^- (aq) to I_2 and not F^- or Cl^- to F_2 or Cl_2.

$$Br_2(l) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(s)$$

Thus, F_2 is the best oxidant.

Among hydrohalic acids, the reducing power decreases as : HI > HBr > HCl > HF. For example, HI and HBr reduce H_2SO_4 to SO_2 while HCl and HF donot.

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$
$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

Similarly, I^- reduces Cu^{2+} to Cu^+ but Br^- does not.

$$2Cu^{2+}\ (aq) + 4I^-\ (aq) \longrightarrow Cu_2I_2\ (s) + I_2(aq)$$

Further among HCl and HF, HCl is a stronger reducing agent than HF because HCl can reduce MnO_2 to Mn^{2+}.

$$MnO_2(s) + 4HCl\ (aq) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O$$

But HF does not reduce MnO_2. Therefore, among hydrohalic acid HI is the strongest reducing agent.

Q. 16. Why does the following reaction occur ?

$$XeO_6^{4-}(aq) + 2F^-(aq) + 6H^+(aq) \longrightarrow XeO_3(g) + F_2(g) + 3H_2O(l)$$

What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction?

Ans. $\overset{+8}{Xe}O_6^{4-}(aq) + 2\overset{-1}{F^-}(aq) + 6H^+(aq) \longrightarrow \overset{+6}{Xe}O_3(s) + \overset{0}{F_2}(g) + 3H_2O(l)$

O.N. of Xe decreases from +8 (in XeO_6^{4-}) to +6 (in XeO_3) and that of F increases from –1 (in F^-) to 0 (in F_2). Therefore, XeO_6^{4-} is reduced while F^- is oxidised. The reaction occurs because Na_4XeO_6 (or XeO_6^{4-}) is a stronger oxidising agent than F_2.

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Q. 17. Consider the reactions :

(a) $H_3PO_2(aq) + 4AgNO_3(aq) + H_2O(l) \longrightarrow H_3PO_4(aq) + 4Ag(s) + 4HNO_3(aq)$

(b) $H_3PO_2(aq) + 2CuSO_4(aq) + H_2O(l) \longrightarrow H_3PO_4(aq) + 2Cu(s) + H_2SO_4(aq)$

(c) $C_6H_5CHO(l) + 2[Ag(NH_3)_2](aq) + 3OH^-(aq) \longrightarrow C_6H_5COO^-(aq) + 2Ag(s) + 4NH_3(aq) + 2H_2O(l)$

(d) $C_6H_5CHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \longrightarrow$ **No change observed.**

What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these ?

Ans. Reaction (*a*) and (*b*) infer that H_3PO_2 (hypophosphorus acid) is a reducing agent and reduces both $AgNO_3$ and $CuSO_4$ to Ag and Cu respectively. This also means that both $AgNO_3$ and $CuSO_4$ act as oxidising agent and oxidise H_3PO_2 to H_3PO_4 (phosphoric acid).

Reaction (*c*) indicate that $[Ag(NH_3)_2]^+$ oxidises C_6H_5CHO (benzaldehyde) to $C_6H_5COO^-$ (benzoate ion) but reaction (d) indicates that Cu^{2+} ions cannot oxidise C_6H_5CHO to $C_6H_5COO^-$. Thus, we can infer from the above reactions that Ag^+ ion is a stronger oxidising agent than Cu^{2+} ion.

Q. 18. Balance the following redox reactions by ion – electron method :

(a) $MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_2(s) + I_2(s)$ **(in basic medium)**

(b) $MnO_4^-(aq) + SO_2(g) \longrightarrow Mn^{2+}(aq) + HSO_4^-(aq)$ **(in acidic solution)**

(c) $H_2O_2(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + H_2O(l)$ **(in acidic solution)**

(d) $Cr_2O_7^{2-} + SO_2(g) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ **(in acidic solution)**

Ans. (*a*) *Refer Solved Example 30. (Page 27).*

(*b*) $\overset{+7}{M}nO_4^-(aq) + \overset{+4}{S}O_2(g) \longrightarrow \overset{+2}{Mn}^{2+}(aq) + \overset{+6}{H}SO_4^-(aq)$

In this reaction, manganese undergoes reduction because oxidation number of Mn decreases from +7(in MnO_4^-) to +2 (in Mn^{2+}). SO_2 gets oxidised because oxidation number of sulphur increases from + 4 (in SO_2) to + 6 in (HSO_4^-).

Oxidation half reaction : $SO_2(g) \longrightarrow HSO_4^-(aq)$

Reduction half reaction : $MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$

Balancing each half reaction separately as :

$$SO_2(g) \longrightarrow HSO_4^-(aq)$$

(*i*) Balance all atoms other than H and O (already done).

(*ii*) Sulphur changes its oxidation number from + 4 to + 6 and there is a difference of 2 electrons. To balance the electrons,

$$SO_2(g) \longrightarrow HSO_4^-(aq) + 2e^-$$

(*iii*) Since the reaction takes place in acidic medium add $3H^+$ on the right hand side and two H_2O molecules on the left hand side.

$$SO_2(g) + 2H_2O(l) \longrightarrow HSO_4^-(aq) + 3H^+ + 2e^-$$

To balance reduction half reaction.

$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$$

(*i*) Balance all atoms other than H and O (already done).

(*ii*) Manganese changes its oxidation number from + 7 to + 2 and there is difference of 5 electrons. To balance the electrons,

$$MnO_4^-(aq) + 5e^- \longrightarrow Mn^{2+}(aq)$$

(*iii*) Since the reaction takes place in acidic medium add $8H^+$ on the left to equate the net charges on both sides and 4 H_2O to the right to balance oxygen atoms.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+}$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

Adding two half reactions by equating the number of electrons.

$$MnO_4^-(aq) + 8H^+ + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)] \times 2$$

$$SO_2(g) + 2H_2O \longrightarrow HSO_4^-(aq) + 3H^+(aq) + 2e^-] \times 5$$

$$2MnO_4^-(aq) + 5SO_2(g) + 2H_2O(l) + H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5\,HSO_4^-(aq)$$

(*c*) $H_2\overset{-1}{O}_2(aq) + \overset{+2}{Fe}^{2+}(aq) \longrightarrow \overset{+3}{Fe}^{3+}(aq) + H_2\overset{-2}{O}(l)$

in acidic medium.

In this reaction, the oxidation number of Fe increases from + 2 (in Fe^{2+}) to +3 (in Fe^{3+}) and therefore, Fe^{2+} has been oxidised. The oxidation number of oxygen has decreased from –1 (in H_2O_2) to – 2 in H_2O and therefore, H_2O_2 has been reduced.

Oxidation half reaction : $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq)$

Reduction half reaction : $H_2O_2(aq) \longrightarrow H_2O(aq)$

These can be balanced by following the steps of balancing as :

Oxidation half reaction :

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq)$$

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^- \quad ...(i)$$

Reduction half reaction

$$H_2O_2(aq) \longrightarrow H_2O(l)$$

$$H_2O_2(aq) + e^- \longrightarrow H_2O(l)$$

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l) \quad ...(ii)$$

Multiply eq (*i*) by 2 and add it to eq. (*ii*) to balance electrons.

$$H_2O_2(aq) + 2Fe^{2+}(aq) + 2H^+ \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

(*d*) $\overset{+6}{Cr}_2O_7^{2-}(aq) + \overset{+4}{S}O_2(g) \longrightarrow \overset{+3}{Cr}^{3+}(aq) + \overset{+6}{S}O_4^{2-}(aq)$

(in acidic medium)

Oxidation half reaction : $SO_2(g) \longrightarrow SO_4^{2-}(aq)$

Reduction half reaction : $Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$

Balancing the oxidation and reduction half reactions separately following the steps of balancing.

Oxidation half reaction :

$$SO_2(g) \longrightarrow SO_4^{2-}(aq)$$

$$SO_2(g) \longrightarrow SO_4^{2-}(aq) + 2e^-$$

$$SO_2(g) + 2H_2O(l) \longrightarrow SO_4^{2-} + 2e^- + 4H^+(aq) \quad ...(i)$$

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Reduction half reaction :

$$Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$$
$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}(aq)$$
$$Cr_2O_7^{2-}(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq)$$
$$Cr_2O_7^{2-}(aq) + 6e^- + 14\,H^+(aq) \longrightarrow 2Cr^{3+}(aq)$$
$$Cr_2O_7^{2-}(aq) + 6e^- + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O \quad ...(ii)$$

Multiply eq. (*i*) by 3 and add it to eq (*ii*) to balance electrons :

$$Cr_2O_7^{2-}(aq) + 3SO_2(g) + 2H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O$$

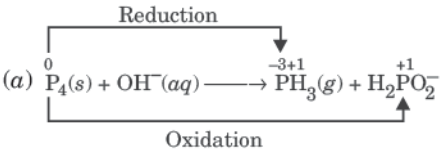
Q. 19. Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent.

(*a*) $P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + H_2PO_2^-(aq)$

(*b*) $N_2H_4(l) + ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(g)$

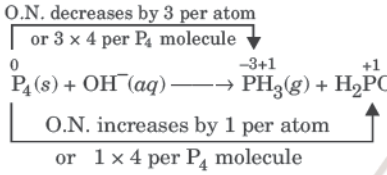
(*c*) $Cl_2O_7(g) + H_2O_2(aq) \longrightarrow ClO_2^-(aq) + O_2(g) + H^+$

Ans. (*a*)



P_4 gets oxidised to $H_2PO_2^-$ and reduced to PH_3 and therefore, P_4 acts as reducing agent as well as oxidising agent.

Oxidation number method



Balance the increase or decrease in oxidation number by multiplying $H_2PO_2^-$ by 3 and PH_3 by 1.

$$P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

To balance O atoms, multiply OH^- by 6,

$$P_4(s) + 6OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

To balance H atoms, add 3 H_2O to L.H.S. and $3OH^-$ on R.H.S, we have

$$P_4(s) + 6OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq) + 3OH^-(aq)$$

or $$P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

Ion electron method

The equation can be split up as

Oxidation half reaction : $P_4(s) \longrightarrow H_2PO_2^-(aq)$

Reduction half reaction : $P_4(s) \longrightarrow PH_3(g)$

These can be balanced separately as :

Oxidation half reaction

$$\overset{0}{P_4}(s) \longrightarrow H_2\overset{+1}{P}O_2^-(aq)$$
$$P_4(s) \longrightarrow 4H_2PO_2^-(aq)$$
$$P_4(s) \longrightarrow 4H_2PO_2^-(aq) + 4e^-$$
$$P_4(s) + 8OH^-(aq) \longrightarrow 4H_2PO_2^-(aq) + 4e^- \quad ...(i)$$

Reduction half reaction

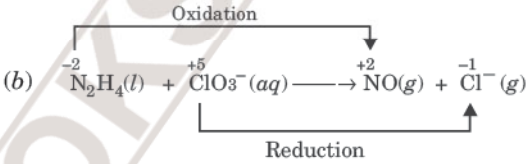
$$\overset{0}{P_4} \longrightarrow \overset{-3}{P}H_3(g)$$
$$P_4(s) \longrightarrow 4PH_3(g)$$
$$P_4(s) + 12e^- \longrightarrow 4PH_3(g)$$
$$P_4(s) + 12e^- \longrightarrow 4PH_3(g) + 12\,OH^-(aq)$$
$$P_4(s) + 12H_2O(l) + 12e^- \longrightarrow 4PH_3(g) + 12\,OH^-(aq) \quad ...(ii)$$

To balance electrons, multiply eq. (*i*) by 3 and add to eq. (*ii*).

$$4P_4(s) + 12OH^-(aq) + 12H_2O(l) \longrightarrow 4PH_3(g) + 12\,H_2PO_2^-(aq)$$

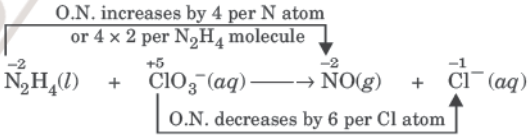
or $$P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

(*b*)



In this reaction, N_2H_4 gets oxidised and acts as a reducing agent and ClO_3^- gets reduced and acts as an oxidising agent.

Oxidation number method



To balance the increase or decrease in oxidation number, multiply N_2H_4 by 3 and ClO_3^- by 4 and add

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(aq)$$

Balance N and Cl atoms on R.H.S.

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq)$$

To balance O atoms add $6H_2O$ molecules on R.H.S.

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq) + 6H_2O$$

Since H atoms are balanced automatically, the above equation represents balanced chemical equation.

Ion electron method

Oxidation half reaction : $N_2H_4(l) \longrightarrow NO(g)$

Reduction half reaction : $ClO_3^-(aq) \longrightarrow Cl^-(aq)$

These can be balanced separately as :

Oxidation half reaction :

$$N_2H_4(l) \longrightarrow NO(g)$$
$$N_2H_4(l) \longrightarrow 2NO(g)$$
$$\overset{-2}{N_2}H_4(l) \longrightarrow 2\overset{+2}{N}O(g) + 8e^-$$
$$N_2H_4(l) + 8OH^-(aq) \longrightarrow 2NO(g) + 8e^- \quad \text{(balancing } OH^- \text{ ions)}$$
$$N_2H_4(l) + 8OH^-(aq) \longrightarrow 2NO(g) + 6H_2O(l) + 8e^- \quad ...(i)$$

Reduction half reaction

$$ClO_3^-(aq) \longrightarrow Cl^-(aq)$$

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$$\overset{+5}{Cl}O_3^- + 6e^- \longrightarrow \overset{-1}{Cl}^-(aq)$$

$$ClO_3^-(aq) + 6e^- \longrightarrow Cl^-(aq) + 6OH^-(aq)$$

$$ClO_3^-(aq) + 3H_2O(l) + 6e^- \longrightarrow Cl^-(aq) + 6\,OH^-(aq) \quad ...(ii)$$

To balance electrons, multiply eq (*i*) by 3 and eq (*ii*) by 4

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4\,Cl^-(aq) + 6H_2O(l)$$

(c) $\overset{+7}{Cl_2O_7}(g) + \overset{-1}{H_2O_2}(aq) \longrightarrow \overset{+3}{ClO_2^-}(aq) + \overset{0}{O_2}(g) + H^+$ (Reduction: Cl_2O_7; Oxidation: H_2O_2)

In this reaction, Cl_2O_7 gets reduced and acts as an oxidising agent while H_2O_2 gets oxidised and acts as a reducing agent.

Oxidation number method

$\overset{+7}{Cl_2O_7}(g) + \overset{-1}{H_2O_2}(aq) \longrightarrow \overset{+3}{ClO_2^-}(aq) + \overset{0}{O_2}(g)$ (O.N. decreases by 4 per atom or 4 × 2 per molecule; O.N. increases by 1 per atom or 1 × 2 per molecule)

To balance the increase or decrease in oxidation number, multiply H_2O_2 by 4 and add

$$Cl_2O_7(g) + 4\,H_2O_2(aq) \longrightarrow ClO_2^-(aq) + O_2(g)$$

Balance Cl atoms and O_2

$$Cl_2O_7(g) + 4H_2O_2(aq) \longrightarrow ClO_2^-(aq) + 4O_2(g)$$

To balance Cl multiply ClO_2^- by 2.

$$Cl_2O_7(g) + 4H_2O_2(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g)$$

To balance O atoms, add $3H_2O$ molecules on R.H.S.

$$Cl_2O_7(g) + 4H_2O_2(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g) + 3H_2O(l)$$

To balance H atoms, add $2H^+$ on R.H.S. since the medium is acidic

$$Cl_2O_7(g) + 4\,H_2O_2(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g) + 3H_2O(l) + 2H^+(aq)$$

Ion electron method

Oxidation half reaction : $\overset{-1}{H_2O_2}(aq) \longrightarrow \overset{0}{O_2}(g)$

Reduction half reaction : $Cl_2O_7(g) \longrightarrow ClO_3^-(aq)$

These can be balanced separately as :

Oxidation half reaction

$$\overset{-1}{H_2O_2}(aq) \longrightarrow O_2(g)$$

$$\overset{-1}{H_2O_2}(aq) \longrightarrow O_2(g) + 2e^-$$

Since the reaction occurs in acidic medium add $2H^+$ on R.H.S. to equate charge,

$$H_2O_2(aq) \longrightarrow O_2(g) + 2e^- + 2H^+(aq) \quad ...(i)$$

Reduction half reaction

$$Cl_2O_7(g) \longrightarrow ClO_2^-(aq)$$

$$Cl_2O_7(g) \longrightarrow 2ClO_2^-(aq)$$

$$Cl_2O_7(g) + 8e^- \longrightarrow 2ClO_2^-(aq)$$

$$Cl_2O_7(g) + 8e^- + 6H^+(aq) \longrightarrow 2ClO_2^-(aq)$$ (medium is acidic)

$$Cl_2O_7(g) + 6H^+(aq) + 8e^- \longrightarrow 2ClO_2^-(aq) + 3H_2O \quad ...(iii)$$

To balance electrons, multiply eq. (*i*) by 4 and add to eq (*ii*)

$$Cl_2O_7(g) + 4\,H_2O_2(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g) + 3H_2O(l) + 2H^+(aq)$$

Q. 20. What sorts of informations can you draw from the following reaction ?

$$(CN)_2(g) + 2OH^-(aq) \longrightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$$

Ans.
(*i*) It is a disproportionation reaction.
(*ii*) The reaction occurs in basic medium.
(*iii*) O.N. of N in $(CN)_2$ is –3 and that in CN^- is –2 and in CNO^- it is –5.
(*iv*) Cyanogen, $(CN)_2$ gets simultaneously reduced to CN^- ion as well as oxidised to cyanate, CNO^- ion.

Q. 21. The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2, and H^+ ion. Write a balanced ionic equation for the reaction.

Ans. The reaction may be written as :

$$Mn^{3+}(aq) \longrightarrow Mn^{2+}(aq) + MnO_2(s) + H^+(aq)$$

This may be balanced as :

Oxidation half equation :

$$\overset{3+}{Mn^{3+}}(aq) \longrightarrow \overset{+4}{Mn}O_2(s)$$

Balance O.N. by adding electrons

$$Mn^{3+}(aq) \longrightarrow \overset{+4}{Mn}O_2(s) + e^-$$

Balance charge by adding H^+ ions

$$Mn^{3+}(aq) \longrightarrow MnO_2(s) + 4H^+ + e^-$$

Balance O atoms by adding H_2O

$$Mn^{3+}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4H^+(aq) + e^- \quad .....(i)$$

Reduction half equation

$$Mn^{3+}(aq) \longrightarrow Mn^{2+}(aq)$$

Balancing O.N. by adding electrons.

$$Mn^{3+}(aq) + e^- \longrightarrow Mn^{2+}(aq) \quad .....(ii)$$

Adding eq. (*i*) and eq. (*ii*)

$$2Mn^{3+}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + Mn^{2+}(aq) + 4H^+(aq)$$

Q. 22. Consider the elements :
Cs, Ne, I and F
(*a*) Identify the element that exhibits only negative oxidation state.
(*b*) Identify the element that exhibits only positive oxidation state.
(*c*) Identify the element that exhibits neither the negative nor does the positive oxidation state.

Ans.
(*a*) F : being most electronegative; shows only a –ve oxidation state of –1.
(*b*) Cs : Alkali metals have only one electron in their valence shell and hence exhibits only +1 oxidation state.
(*c*) I : because of the presence of 7 electrons in its valence shell, I shows O.S of –1 (to have stable noble gas configuration) and +ve oxidation states of +1, +3, +5 and +7 because of the presence of *d*-orbitals.
(*d*) Ne : It is an inert gas and therefore, does not exhibit –ve or +ve O.S.

Q. 23. Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur

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dioxide. Present a balanced equation for this redox change taking place in water.

Ans. The skeletal equation is :

$Cl_2(g) + SO_2(aq) + H_2O(l) \longrightarrow Cl^-(aq) + SO_4^{2-}(aq)$

Reduction half equation :

$$Cl_2(aq) \longrightarrow Cl^-(aq)$$

Balancing Cl atoms

$$Cl_2(aq) \longrightarrow 2Cl^-(aq)$$

Balancing O.N. by adding electrons :

$$\overset{0}{Cl_2}(aq) + 2e^- \longrightarrow 2Cl^-(aq) \qquad ....(i)$$

Oxidation half equation :

$$SO_2(aq) \longrightarrow SO_4^{2-}(aq)$$

Balancing O.N. by adding electrons

$$\overset{+4}{SO_2}(aq) \longrightarrow \overset{+6}{SO_4^{2-}}(aq) + 2e^-$$

Balancing charge by adding H^+ ions

$$SO_2(aq) \longrightarrow SO_4^{2-}(aq) + 2e^- + 4H^+(aq)$$

Balancing O atoms by adding H_2O

$$SO_2(aq) + 2H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2e^- + 4H^+(aq) \qquad ....(ii)$$

Adding equations (i) and (ii) we get

$$Cl_2(aq) + SO_2(aq) + 2H_2O(l) \longrightarrow 2Cl^-(aq) + SO_4^{2-}(aq) + 4H^+(aq)$$

Q. 24. Refer to the periodic table given in your book and now answer the following questions :

(a) Select the possible non-metals that can show disproportionation reaction.

(b) Select three metals that can show disproportionation reaction.

Ans. (a) Non-metals showing disproportionation reactions are : P_4, Cl_2 and S_8

$$\overset{0}{P_4}(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow \overset{-3}{PH_3}(g) + 3\overset{+3}{H_2PO_2^-}(aq)$$

$$\overset{0}{Cl_2}(aq) + 2OH^-(aq) \longrightarrow \overset{-1}{Cl^-}(aq) + \overset{+1}{ClO^-}(aq) + H_2O(l)$$

$$\overset{0}{S_8}(s) + 12OH^-(aq) \longrightarrow \overset{-2}{S}(aq) + 2\overset{+2}{S_2O_3^{2-}} + 6H_2O(l)$$

(b) Metals exhibiting disproportionation reactions are :

Cu^+, Ga^+ In^+

$$\overset{+1}{2Cu^+}(aq) \longrightarrow \overset{+2}{Cu^{2+}}(aq) + \overset{0}{Cu}(s)$$

$$\overset{+1}{3Ga^+}(aq) \longrightarrow \overset{+3}{Ga^{3+}}(aq) + \overset{0}{2Ga}(s)$$

$$\overset{+1}{3In^+}(aq) \longrightarrow \overset{+3}{In^{3+}}(aq) + \overset{0}{2In}(s)$$

Q. 25. In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.00 g. of ammonia and 20.00 g of oxygen ?

Ans. $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

4×17 5×32 4×30

$= 68$ g $= 160$ g $= 120$ g

160 g of O_2 will react with 68 g of NH_3

20 g of O_2 will react with $NH_3 = \dfrac{68}{160} \times 20$

$= 8.5$ g

$\therefore$ O_2 is a limiting reagent.

160 g of O_2 produces NO = 120 g

20 g of O_2 will produces NO $= \dfrac{120}{160} \times 20$

$= 15$ g

Q. 26. Using the standard electrode potentials given in the Table 8.1, predict if the reaction between the following is feasible :

(a) $Fe^{3+}(aq)$ and $I^-(aq)$

(b) $Ag^+(aq)$ and $Cu(s)$

(c) $Fe^{3+}(aq)$ and $Cu(s)$

(d) $Ag(s)$ and $Fe^{3+}(aq)$

(e) $Br_2(aq)$ and $Fe^{2+}(aq)$.

Ans. (a) It is clear from the table that electrode potential $Fe^{3+} \mid Fe$ (0.77V) is more than that of $I_2 \mid I^-$ (0.54V), therefore, Fe^{3+} will be readily reduced and the following reaction is feasible.

$$Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2(s)$$

(b) The electrode potential of $Ag^+ \mid Ag$ (0.80V) is more than that of $Cu^{2+} \mid Cu$ (0.34V) and therefore, Ag^+ will be reduced by copper. The following reaction is feasible.

$$2Ag^+(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$$

(c) The electrode potential of $Fe^{3+} \mid Fe$ (0.77V) is more than that of $Cu^{2+} \mid Cu$ (0.34V), therefore, Fe^{3+} can be reduced . The following reaction is feasible.

$$Fe^{3+}(aq) + Cu(s) \longrightarrow Fe^{2+}(aq) + Cu^{2+}(aq)$$

(d) The electrode potential of $Ag \mid Ag^+$ (0.80V) is more than that of $Fe^{3+} \mid Fe$ (0.77V) and therefore, Ag^+ will not be reduced by Fe^{3+}. Therefore, the reaction will not be feasible.

$$Ag(s) + Fe^{3+}(aq) \longrightarrow 2Ag(aq) + Fe^{2+}(aq)$$

(e) The electrode potential of $Br \mid Br^-$ (1.09V) is more than that of $Fe^{3+} \mid Fe^{2+}$ (0.77V) and therefore, Br will be able to reduce by Fe^{3+}. Therefore, the following reaction is feasible.

$$\frac{1}{2}Br_2(aq) + Fe^{2+}(aq) \longrightarrow Br^-(aq) + Fe^{3+}(aq)$$

Q. 27. Predict the products of electrolysis in each of the following :

(i) An aqueous solution of $AgNO_3$ with silver electrodes

(ii) An aqueous solution of $AgNO_3$ with platinum electrodes

(iii) An aqueous solution of H_2SO_4 with platinum electrodes

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes

Ans. (i) Electrolysis of aqueous solution of $AgNO_3$ using silver electrodes :

$$AgNO_3(s) + nH_2O \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : Ag^+ ions have lower discharge potential than H^+ ions.

Hence Ag^+ ions will be deposited as silver (in preference to H^+ ions).

At anode : Since silver electrode is attacked by NO_3^- ions, Ag anode will dissolve to form Ag^+ ions in the solution.

$$Ag \longrightarrow Ag^+ + e^-$$

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(*ii*) Electrolysis of aqueous solution of $AgNO_3$ using platinum electrodes :

At cathode : same as above.

At anode : Since silver is not attackable, out of OH^- and NO_3^- ions, OH^- ions have lower discharge potential and hence OH^- ions will be discharged in preference to NO_3^-. The OH^- will decompose to give O_2.

$$OH^-(aq) \longrightarrow OH + e^-$$
$$4OH^-(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

(*iii*) Electrolysis of H_2SO_4 with Pt electrodes :

$$H_2SO_4\ (aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : $H^+ + e^- \longrightarrow H$

$$H + H \longrightarrow H_2(g)$$

At anode : $OH^- \longrightarrow OH + e^-$

$$4OH \longrightarrow 2H_2O + O_2(g)$$

(*iv*) Electrolysis of aqueous solution of $CuCl_2$ with platinum electrodes :

$$CuCl_2\ (s) + (aq) \longrightarrow Cu^{2+}(aq) + 2Cl^-(aq)$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : Cu^{2+} will be reduced in preference to H^+ ions.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

At anode : Cl^- ions will be oxidised in preference to OH^- ions

$$Cl^- \longrightarrow Cl + e^-$$
$$Cl + Cl \longrightarrow Cl_2$$

Thus copper will be deposited on the cathode and Cl_2 will be liberated at anode.

Q. 28. Arrange the following metals in the order in which they displace each other from the solution of their salts.
Al, Cu, Fe, Mg and Zn.

Ans. Mg, Al, Zn, Fe, Cu

Q. 29. Given the standard electrode potentials,
$K^+ | K = -2.93V$, $Ag^+ | Ag = 0.80V$,
$Hg^{2+} | Hg = 0.79$ V
$Mg^{2+} | Mg = -2.37V$, $Cr^{3+} | Cr = -0.74V$
arrange these metals in their increasing order of reducing power.

Ans. $Ag^+ | Ag$, $Hg^{2+} | Hg$, $Cr^{3+} | Cr$, $Mg^{2+} | Mg$, $K^+ | K$

Q. 30. Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show :
(*i*) which of the electrode is negatively charged,
(*ii*) the carriers of the current in the cell, and
(*iii*) individual reaction at each electrode.

Ans. The cell may be depicted similar to Fig. 8.3. The cell may be represented as

$Zn(s) | Zn^{2+}(aq) \| Ag^+(aq) | Ag(s)$

(*i*) Zinc electrode (anode)

(*ii*) Current will flow from silver to zinc in the external circuit.

(*iii*) **At anode :** $Zn\ (s) \longrightarrow Zn^{2+}(aq) + 2e^-$

At cathode : $Ag^+\ (aq) + e^- \longrightarrow Ag(s)$

NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 72*

Short Answer Questions *Carrying 2 or 3 marks*

Q. 1. The reaction $Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$ represents the process of bleaching. Identify and name the species that bleaches the substances due to its oxidising action.

Ans.
$$\overset{0}{Cl_2}(g) + 2OH^-(aq) \longrightarrow \overset{+1}{Cl}O^-(aq) + \overset{-1}{Cl^-}(aq) + H_2O(l)$$

In this reaction, O.N. of Cl increases from 0 (in Cl_2) to +1(in ClO^-) and decreases to –1(in Cl^-). Therefore, Cl_2 is both oxidised to ClO^- and reduced to Cl^-. Since Cl^- ion cannot act as an oxidising agent (because it cannot decrease its O.N. lower than –1), therefore, Cl_2 bleaches substances due to oxidising action of hypochlorite, ClO^-, ion.

Q. 2. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.

Ans. In MnO_4^-, Mn is in the highest oxidation state (+7). Therefore, it cannot be oxidised further and hence does not undergo disproportionation. However, in MnO_4^{2-}, Mn is in +6 oxidation state. Therefore, it can increase its O.N to + 7 and decrease its O.N. to some lower value. Thus, it undergoes disproportionation as :

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Here O.N. of Mn increases from +6 (in MnO_4^{2-}) to +7 (in MnO_4^-) and decreases to +4(in MnO_2).

Q. 3. PbO and PbO_2 react with HCl according to following chemical equations :

$$2PbO + 4HCl \longrightarrow 2PbCl_2 + 2H_2O$$
$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$$

Why do these compounds differ in their reactivity ?

Ans. (*i*)
$$\overset{+2}{PbO} + 4HCl \longrightarrow \overset{+2}{PbCl_2} + 2H_2O$$
$$\overset{+4}{PbO_2} + 4HCl \longrightarrow \overset{+2}{PbCl_2} + \overset{0}{Cl_2} + 2H_2O$$

In reaction (*i*), O.N. of none of the atoms undergo a change. Therefore, it is not a redox reaction. It is an acid-base reaction, because PbO_2 is a basic oxide which reacts with HCl acid.

The reaction (*ii*) is a redox reaction in which PbO_2 gets reduced and acts as an oxidising agent.

Q. 4. Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2. Explain why ?

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Ans. PbO is a basic oxide and therefore, it reacts with nitric acid. It is a simple acid-base reaction between PbO and HNO_3.

$$2PbO + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O$$

(Acid-base reaction)

On the other hand in PbO_2, lead is in +4 oxidation state and cannot be oxidised further. Therefore PbO_2 is passive towards HNO_3 and no reaction takes place.

Q. 5. Write balanced chemical equations for the following reactions :

(*i*) Permanganate ion (MnO_4^-) reacts with sulphur dioxide gas in acidic medium to produce Mn^{2+} and hydrogen sulphate ion. (Balance by ion electron method)

(*ii*) Reaction of liquid hydrazine (N_2H_4) with chlorate ion (ClO_3^-) in basic medium produces nitric oxide gas and chloride ion in gaseous state. (Balance by oxidation number method)

(*iii*) Dichlorine heptaoxide (Cl_2O_7) in gaseous state combines with an aqueous solution of hydrogen peroxide in acidic medium to give chlorite ion (ClO_2^-) and oxygen gas. (Balance by ion electron method)

Ans. (*i*) $MnO_4^-(aq) + SO_2(g) \longrightarrow Mn^{2+}(aq) + HSO_4^-(aq)$ in acidic medium

Refer NCERT Textbook Exercises Q. 18(b).

(*ii*) $N_2H_4(l) + ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(aq)$

Refer NCERT Textbook Exercises Q. 19(b).

(*iii*) $Cl_2O_7(g) + H_2O_2(aq) \longrightarrow ClO_2^-(aq) + O_2(g) + H^+$

Refer NCERT TextBook Exercises Q. 19(c).

Q. 6. Calculate the oxidation number of phosphorus in the following species.

(*a*) HPO_3^{2-} and (*b*) PO_4^{3-}

Ans. (*a*) Let O.N. of P be x

$$\overset{+1}{H}\ \overset{x}{P}\ \overset{3(-2)}{O_3^{2-}}$$

$$+1 + x + 3(-2) = -2 \quad \text{or } x = +3$$

(*b*)

$$\overset{x}{P}O_4^{3-}$$

$$x + 4(-2) = -3 \quad \text{or } x = +5$$

Q. 7. Calculate the oxidation number of each sulphur atom in the following compounds :

(*a*) $Na_2S_2O_3$ (*b*) $Na_2S_4O_6$

(*c*) Na_2SO_3 (*d*) Na_2SO_4

Ans. Let O.N. of S be x

(*a*) $Na_2\overset{x}{S}_2O_3$

$$2(+1) + 2(x) + 3(-2) = 0 \text{ or } 2x = +4 \text{ or } x = +2$$

(*b*) *2.5, Refer Solved Example 6 (ii) page 10.*

(*c*) $Na_2\overset{x}{S}O_3$

$$2(+1) + x + 3(-2) = 0 \text{ or } x = +4$$

(*d*) $Na_2\overset{x}{S}O_4$

$$2(+1) + x + 4(-2) = 0 \text{ or } x = +6$$

Q. 8. Balance the following equations by the oxidation number method.

(*i*) $Fe^{2+} + H^+ + Cr_2O_7^{2-} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(*ii*) $I_2 + NO_3^- \longrightarrow NO_2 + IO_3^-$

(*iii*) $I_2 + S_2O_3^{2-} \longrightarrow I^- + S_4O_6^{2-}$

(*iv*) $MnO_2 + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$

Ans. Try yourself. Balanced equations are

(*i*) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(*ii*) $I_2 + 10NO_3^- + 8H^+ \longrightarrow 10NO_2 + 2IO_3^- + 4H_2O$

(*iii*) $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

(*iv*) $MnO_2 + C_2O_4^{2-} + 4H^+ \longrightarrow Mn^{2+} + 2CO_2 + 2H_2O$

Q. 9. Identify the redox reactions out of the following reactions and identify the oxidising and reducing agents in them.

(*i*) $3HCl(aq) + HNO_3(aq) \longrightarrow Cl_2(g) + NOCl(g) + 2H_2O(l)$

(*ii*) $HgCl_2(aq) + 2KI(aq) \longrightarrow HgI_2(s) + 2KCl(aq)$

(*iii*) $Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$

(*iv*) $PCl_3(l) + 3H_2O(l) \longrightarrow 3HCl(aq) + H_3PO_3(aq)$

(*v*) $4NH_3 + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(g)$

Ans. (*i*) Writing the O.N. of on each atom,

$$\overset{+1\ -1}{3HCl(aq)} + \overset{+1\ +5\ -2}{HNO_3(aq)} \longrightarrow \overset{0}{Cl_2(g)} + \overset{+3\ -2}{NO}\overset{-1}{Cl(g)} + \overset{+1\ -2}{2H_2O(l)}$$

Here, O.N. of Cl increases from –1 (in HCl) to 0 (in Cl_2). Therefore, Cl^- is oxidised and hence HCl acts as a reducing agent.

The O.N. of N decreases from + 5 (in HNO_3) to +3 (in NOCl) and therefore, HNO_3 acts as an oxidising agent.

Thus, reaction (*i*) is a redox reaction.

(*ii*) $\overset{+2\ -1}{HgCl_2(aq)} + 2K\overset{+1\ -1}{I(aq)} \longrightarrow \overset{+2\ -1}{HgI_2(s)} + 2K\overset{+1\ -1}{Cl(aq)}$

Here O.N. of none of the atoms undergo a change and therefore, this is not a redox reaction.

(*iii*) $\overset{+3\ -2}{Fe_2O_3(s)} + \overset{+2\ -2}{3CO(g)} \xrightarrow{\Delta} \overset{0}{2Fe(s)} + \overset{+4\ -2}{3CO_2(g)}$

Here, O.N. of Fe decreases from +3 (in Fe_2O_3) to 0 (in Fe) and therefore, Fe_2O_3 acts as an oxidising agent.

O.N. of C increases from +2 (in CO) to +4 (in CO_2) and therefore, CO acts as a reducing agent.

Thus, this is a redox reaction.

(*iv*) $\overset{+3\ -1}{PCl_3(l)} + 3H_2O(l) \longrightarrow 3HCl(aq) + \overset{+1\ +3\ -2}{H_3PO_3(aq)}$

Here O.N. of none of the atoms undergo a change and therefore, it is not a redox reaction.

(*v*) $\overset{-3\ +1}{4NH_3(g)} + \overset{0}{3O_2(g)} \longrightarrow \overset{0}{2N_2(g)} + \overset{+1\ -2}{6H_2O(g)}$

Here O.N. of N increases from –3 (in NH_3) to 0 in (N_2) and therefore, NH_3 acts as a reducing agent.

O.N. of O decreases from 0 (in O_2) to –2(in H_2O) and therefore, O_2 acts as an oxidising agent.

Thus, reaction (*v*) is a redox reaction.

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Q. 10. Balance the following ionic equations

(*i*) $Cr_2O_7^{2-} + H^+ + I^- \longrightarrow Cr^{3+} + I_2 + H_2O$

(*ii*) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(*iii*) $MnO_4^- + SO_3^{2-} + H^+ \longrightarrow Mn^{2+} + SO_4^{2-} + H_2O$

(*iv*) $MnO_4^- + H^+ + Br^- \longrightarrow Mn^{2+} + Br_2 + H_2O$

Ans. (*i*) Reduction

$\overset{+6}{Cr_2O_7^{2-}} + H^+ + \overset{-1}{I^-} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{0}{I_2} + H_2O$

Oxidation

Dividing the equation into two half reactions :

Oxidation half reaction : $I^- \longrightarrow I_2$

Reduction half reaction : $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Balancing oxidation and reduction half reactions separately as :

Oxidation half reaction

$$I^- \longrightarrow I_2$$
$$2I^- \longrightarrow I_2$$
$$2I^- \longrightarrow I_2 + 2e^- \quad ...(i)$$

Reduction half reaction

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$
$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$
$$Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+}$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad ...(ii)$$

(acidic medium)

To balance the electrons, multiply eq(*i*) by 3 and add to eq (*ii*)

$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(*ii*) *Refer Solved Example 25 (Page 908).*

(*iii*) Reduction

$\overset{+7}{MnO_4^-} + \overset{+4}{SO_3^{2-}} \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+6}{SO_4^{2-}} + H_2O$

Oxidation

Dividing the equation into two half reactions :

Oxidation half reaction : $SO_3^{2-} \longrightarrow SO_4^{2-}$

Reduction half reaction : $MnO_4^- \longrightarrow Mn^{2+}$

Balancing oxidation and reduction half reactions separately as :

Oxidation half reaction

$$SO_3^{2-} \longrightarrow SO_4^{2-}$$
$$SO_3^{2-} \longrightarrow SO_4^{2-} + 2e^-$$

Since the reaction occurs in acidic medium,

$$SO_3^{2-} \longrightarrow SO_4^{2-} + 2e^- + 2H^+$$
$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^- \quad ....(i)$$

Reduction half reaction

$$MnO_4^- \longrightarrow Mn^{2+}$$
$$MnO_4^- + 5e^- \longrightarrow Mn^{2+}$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+}$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad ...(ii)$$

To balance the electrons, multiply eq. (*i*) by 5 and eq. (*ii*) by 2 and add

$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

(*iv*) Reduction

$\overset{+7}{MnO_4^-} + H^+ + \overset{-1}{Br^-} \longrightarrow \overset{+2}{Mn^{2+}} + \overset{0}{Br_2} + H_2O$

Oxidation

Dividing the equation into two half reactions :

Oxidation half reaction : $Br^- \longrightarrow Br_2$

Reduction half reaction : $MnO_4^- \longrightarrow Mn^{2+}$

Balancing oxidation and reduction half reaction separately as :

Oxidation half reaction

$$Br^- \longrightarrow Br_2$$
$$2Br^- \longrightarrow Br_2$$
$$2Br^- \longrightarrow Br_2 + 2e^- \quad ...(i)$$

Reduction half reaction

$$MnO_4^- \longrightarrow Mn^{2+}$$
$$MnO_4^- + 5e^- \longrightarrow Mn^{2+}$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+}$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad ...(ii)$$

To balance the electrons, multiply eq.(*i*) by 5 and eq.(*ii*) by 2 and add

$2MnO_4^- + 10Br^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Br_2 + 8H_2O$

Long Answer Questions *Carrying 5 marks*

Q. 11. Explain redox reactions on the basis of electron transfer. Give suitable examples.

Ans. *Refer Text (Page 3–4).*

Q. 12. On the basis of standard electrode potential values, suggest which of the following reactions would take place ? (Consult the book for E° value).

(*i*) $Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$

(*ii*) $Mg + Fe^{2+} \longrightarrow Mg^{2+} + Fe$

(*iii*) $Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$

(*iv*) $Fe + Cd^{2+} \longrightarrow Cd + Fe^{2+}$

Ans. (*i*) $Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$

$E°(Cu^{2+}|Cu) = +0.34V$, $E°(Zn^{2+}|Zn) = -0.76V$

$E^o_{cell} = E°(cathode) - E°(anode)$

$= -0.76 - 0.34 = -1.10V$

Since E^o_{cell} is –ve, the reaction does not occur.

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(*ii*) $Mg + Fe^{2+} \longrightarrow Mg^{2+} + Fe$

$E^\circ(Mg^{2+}|Mg) = -2.37V$, $E^\circ(Fe^{2+}|Fe) = -0.74V$

$$E^\circ_{cell} = -0.74 - (-2.37) = +1.63V$$

Since E°_{cell} is +ve, the reaction will take place.

(*iii*) $Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$

$$E^\circ_{cell} = +1.08 - 1.36 = -0.28V$$

Since E°_{cell} is –ve, this reaction does not occur.

(*iv*) $Fe + Cd^{2+} \longrightarrow Cd + Fe^{2+}$

$$E^\circ_{cell} = -0.44 - (-0.74) = +0.30$$

Since E°_{cell} is +ve, therefore, this redox reaction will occur.

Q. 13. Why does fluorine not show disproportionation reaction ?

Ans. Fluorine is most electronegative and strongest oxidising agent and therefore, it does not show positive oxidation states.

Q. 14. Write redox couples involved in the reactions (*i*) to (*iv*) given in Q. 12.

Ans. (*i*) $Cu^{2+}|Cu$ and $Zn^{2+}|Zn$

(*ii*) $Mg^{2+}|Mg$ and $Fe^{2+}|Fe$

(*iii*) $Br_2|Br^-$ and $Cl_2|Cl^-$

(*iv*) $Fe^{2+}|Fe$ and $Cd^{2+}|Cd$

Q. 15. Find out the oxidation number of chlorine in the following compounds and arrange them in increasing order of oxidation number of chlorine : $NaClO_4$, Na_2CO_3, NaClO, $KClO_2$, Cl_2O_7, ClO_3, Cl_2O, NaCl, Cl_2, ClO_2.

Which oxidation state is not present in any of the above compounds ?

Ans. Let oxidation state of Cl be x

$NaClO_4$	$+1 + x + 4(-2) = 0$	or $x = +7$
$NaClO_3$	$+1 + x + 3(-2) = 0$	or $x = +5$
NaClO	$+1 + x + -2 = 0$	or $x = +1$
$KClO_2$	$+1 + x + 2(-2) = 0$	or $x = +3$
Cl_2O_7	$2x + 7(-2) = 0$	or $x = +7$
ClO_3	$x + 3(-2) = 0$	or $x = +6$
Cl_2O	$2x - 2 = 0$	or $x = +1$
NaCl	$+1 + x = 0$	or $x = -1$
Cl_2	$2x = 0$	or $x = 0$
ClO_2	$x + 2(-2) = 0$	or $x = +4$

None of the compounds have an O.N. of +2.

Q. 16. Which method can be used to find out the strength of reductant/oxidant in a solution ? Explain with an example.

Ans. The method to find out the strength of reductant/oxidant in a solution, is to connect the redox couple of that species to normal hydrogen electrode and measure its electrode potential.

If E° is +ve, the electrode acts as reductant and if it is –ve, the electrode acts as oxidant. In this way by measuring the value for different redox couples, the comparative strength can be determined.

QUICK MEMORY TEST

A. Say True or False

1. The oxidation state of oxygen is always –2.
2. Oxidation number of an element can be zero but valency is never zero.
3. The decomposition of calcium carbonate to calcium oxide and carbon dioxide is a redox reaction.
4. Nitrous acid can act both as an oxidising as well as reducing agent.
5. The reaction : $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$ cannot be regarded as a redox reaction.
6. The oxidation number of each iron atom in Fe_3O_4 is same.
7. The reaction : $V_2O_5 + 5Ca \longrightarrow 2V + 5CaO$ is a metal displacement reaction.
8. The oxidation number of carbon in CH_2Cl_2 is +4.
9. Oxidation number of Mn in MnO_4^- is more than in MnO_2.
10. The oxidation number of hydrogen in LiH is –1.

B. Complete the missing links

1. The oxidation number of chromium in CrO_5 is .....
2. Oxidant is a substance in which the oxidation number of one of the atoms .....
3. When the oxidation number of an element is maximum, it can act only as .....
4. The oxidation number of oxygen in sodium peroxide is .....
5. In an electrochemical cell ..... acts as a negative pole and ..... acts as a positive pole.
6. A compound in which oxidation number of oxygen is +2 is .....
7. In an electrochemical cell, oxidation occurs at ..... and reduction occurs at .....

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8. Stock notation of chromium trioxide is .....
9. Oxidation number of N in ammonium sulphate is .....
10. Oxidation number of chlorine in Cl_2O_7 is .....

C. Choose the correct alternative

1. In an electrochemical cell reduction occurs at *cathode / anode.*
2. In an oxidation reaction, oxidation number of an atom *increases / decreases.*
3. Oxidation number of C in CO_2 is *more / less* than in CH_2Cl_2.
4. Oxidation number of phosphorus in Na_3PO_4 is *+3 / +5.*
5. The oxidation number of each terminal S atom in tetrathionate ion is *+5 / +2.5.*
6. In the reaction : $F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O$, F_2 undergoes *only reduction / both oxidation and reduction.*
7. Copper metal *can / cannot* be oxidised by Zn^{2+} ions.
8. Iodine oxidises $Na_2S_2O_3$ to $Na_2S_4O_6$. This statement is *true / false.*
9. Reductant is a substance in which oxidation number of one of the atoms *decreases / increases.*
10. In the reaction $Zn(s) + PbCl_2(aq) \longrightarrow Pb(s) + ZnCl_2(aq)$, zinc acts as *oxidising / reducing* agent.

Answers QUICK MEMORY TEST

A. Say True or False

1. False
2. True
3. **False :** It is not a redox reaction because oxidation number of none of the atoms changes.
4. True
5. True
6. **False :** It exists as $FeO{\cdot}Fe_2O_3$ having oxidation number +2 and +3.
7. True
8. **False :** It is zero.
9. True
10. True.

B. Complete the missing links

1. 5
2. decreases
3. oxidising agent
4. –1
5. anode, cathode
6. OF_2
7. anode, cathode
8. $Cr_2(III)O_3$
9. – 3
10. +7

C. Choose the correct alternative

1. cathode
2. increases
3. more
4. +5
5. +5
6. only reduction
7. cannot
8. true
9. increases
10. reducing

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q. 1.While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act as oxidising agents. Why ?

Ans. The oxidation state of S in SO_2 is +4. It can be oxidised to +6 oxidation state or reduced to +2. Therefore, it acts as a reducing agent as well as oxidising agent. Similarly, the oxidation state of oxygen in H_2O_2 is –1. It can be oxidised to O_2 (zero oxidation state) or reduced to H_2O or OH^-(–2 oxidation state) and therefore acts as reducing as well as oxidising agent.

However, both ozone and nitric acid can only decrease their oxidation number and therefore, act only as oxidising agents.

Q. 2.Out of aluminium and silver vessel, which one will be more suitable to store 1 M HCl solution and why ?

$$E^\circ_{Al^{3+}|Al} = -1.66\ V,\ E^\circ_{Ag^+|Ag} = +0.80\ V.$$

Ans. Since reduction potential of silver is more than that of hydrogen ($E^\circ_{H^+|H_2}$, Pt = 0), silver vessel will be suitable to store 1M HCl. On the other hand, $E^\circ_{Al^{3+}|Al}$ is less than that of hydrogen ($E^\circ_{H^+|H_2}$,Pt) so that hydrogen will be liberated if stored in aluminium vessel.

Q. 3.Can Fe^{3+} oxidize Br^- to Br_2 at 1 M concentration?

$$E^\circ(Fe^{3+} | Fe^{2+}) = 0.77\ V \text{ and } E^\circ(Br | Br^-) = 1.09\ V$$

Ans.$E^\circ(Fe^{3+} | Fe^{2+})$ is lower than that of $E^\circ(Br | Br^-)$. Therefore, Fe^{2+} can reduce Br_2 but Br^- cannot reduce Fe^{3+}. Thus, Fe^{3+} cannot oxidise Br^- to Br_2.

Q.4. Is it safe to stir 1M $AgNO_3$ solution with a copper spoon ? Given :

$$E^\circ_{Ag^+|Ag} = 0.80\ V,\ E^\circ_{Cu^{2+}|Cu} = 0.34V.$$

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Ans. No, copper spoon will dissolve as Cu^{2+} ions because copper has more tendency to get oxidised than silver.

Q.5. Consider the following table of standard reduction potentials :

Reaction	E°(V)
$A^{3+} + 2e^- \longrightarrow A^+$	1.36
$B^{2+} + 2e^- \longrightarrow B$	0.72
$C^{2+} + 2e^- \longrightarrow C$	–0.28
$D^+ + e^- \longrightarrow D$	–1.42

(*a*) Which substance is

(*i*) strongest oxidising agent ?

(*ii*) strongest reducing agent ?

(*b*) Which substance can be oxidised by B^{2+} ?

(*c*) Which substance can be reduced by C ?

(*d*) Write a balanced chemical equation for the overall cell reaction that gives the highest cell voltage and calculate E° for the reaction.

Ans. (*a*) (*i*) A^{3+} is the strongest oxidising agent.

(*ii*) D is the strongest reducing agent.

(*b*) B^{2+} can oxidise C and D.

(*c*) C can reduce A^{3+} and B^{2+}.

(*d*) $A^{3+} + 2D \longrightarrow A^+ + 2D^+$

$E^\circ = 1.36 - (-1.42) = 2.78$ V

Q.6. Copper dissolves in dilute HNO_3 but not in dilute HCl. Explain.

Ans. Since E° of $Cu^{2+}|Cu$ electrode (+0.34 V) is higher than that of $H^+|\frac{1}{2}H_2$ (0.0V), therefore, H^+ ions cannot oxidise Cu to Cu^{2+} ions and consequently, copper does not dissolve in dil. HCl. On the other hand, the electrode potential of NO_3^- ion, $NO_3^-|NO$ (+0.97V) is higher than that of copper electrode and hence, it can oxidise Cu to Cu^{2+} and hence copper dissolves in dil. HNO_3.

Q.7. Element A will reduce the cation of element B (B^+) but will not reduce the cation of element C (C^+). Will element C reduce the cation of element B? Explain.

Ans. Since A will reduce B^+, B has higher reduction potential than A and therefore, B lies above A in the electrochemical series. Now, A will not reduce C^+, C has lower reduction potential than A and therefore, C lies below A in the electrochemical series. Therefore, C must be below B in the series and hence C will reduce B^+.

Q.8.Why does an electrochemical cell stops working after some time ?

Ans. The electrode potential of any electrode depends upon the concentration of ions. With time as the cell operates, the concentrations of ions in different compartments change and therefore, the electrode potentials also change. For example, in Zn–Cu cell,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+} + Cu(s)$$

the concentration of the Zn^{2+} ions in the anode compartment increases and hence the electrode potential of anode also increases. At the same time, the concentration of Cu^{2+} ions in the cathode compartment decreases and hence the electrode potential of the cathode also decreases. Ultimately, the electrode potential of the two electrodes become equal and at this stage, the cell stops working because E_{cell} (difference of electrode potentials of the cathode and anode) becomes zero.

Q.9. (*a*) What is the maximum and minimum oxidation states of nitrogen in its compounds ? Give one example each.

(*b*) What is the oxidation number of N in each of the following :

(*i*) NH_3 (*ii*) N_2H_4 (*iii*) HN_3 (*iv*) NO_2^- (*v*) N_2O (*vi*) HCN (*vii*) N_2 (*viii*) NH_2OH (*ix*) HNO_3 (*x*) NO_2.

(*c*) What is the oxidation state of hydrogen in each of the following :

(*i*) H^+ (*ii*) H_2 (*iii*) $LiAlH_4$ (*iv*) HCl (*v*) LiH

Ans. (*a*) +5 equal to group number (e.g. N_2O_5) and –3 equal to the group number minus 8 (e.g. NH_3)

(*b*) (*i*) –3 (*ii*) –2 (*iii*) –1/3 (*iv*) +3 (*v*) +1 (*vi*) –3 (*vii*) 0 (*viii*) –1 (*ix*) +5 (*x*) +4

(*c*) (*i*) +1 (*ii*) 0 (*iii*) –1 (*iv*) +1 (*v*) –1

Q.10. (*a*) Use the following reactions to arrange the elements A, B, C and D in order of their redox reactivity :

(*i*) $A + B^+ \longrightarrow A^+ + B$

(*ii*) $B + D^+ \longrightarrow B^+ + D$

(*iii*) $C^+ + D \longrightarrow$ No reaction

(*iv*) $B + C^+ \longrightarrow B^+ + C$

(*b*) On the basis of above redox activity series, predict which of the following reactions would you expect to occur.

(*i*) $A^+ + C \longrightarrow A + C^+$ (*ii*) $A^+ + D \longrightarrow A + D^+$

Ans. (*a*) The electrochemical series or redox activity is based on the decreasing order of reduction potentials. This means that the species which gets reduced is higher in the electrochemical series as compared to the other which is to get oxidised (lose electrons).

In reaction (*i*), B^+ gets reduced by A and therefore B is higher than A in electrochemical series.

In reaction (*ii*) D^+ gets reduced by B and therefore, D is higher in electrochemical series than B. In reaction (*iii*) C^+ does not get reduced by D, therefore, C is lower than D in electrochemical series. But according to reaction (*iv*) C^+ gets reduced by B and therefore, C is higher in electrochemical series than B. Thus, the correct order is

$$D > C > B > A$$

(*b*) Both reactions donot occur because A cannot be reduced by C as well as D.

Q.11. 40.05 mL of 1.0 M Ce^{4+} are required to titrate 20.0 mL of 1.0 M Sn^{2+} to Sn^{4+}. What is the oxidation state of cerium in the reduction product ?

Ans. The reactions occuring are :

$$Ce^{4+} + ne^- \longrightarrow Ce^{(4-n)+}$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

To balance the equations, (the no. of electrons lost = no. of electrons gained) multiply eq. (i) by 2 and eq. (ii) by n and add

$$2Ce^{4+} + nSn^{2+} \longrightarrow Ce^{(4-n)+} + Sn^{4+}$$

Moles of Ce^{4+} in 40.05 mL of 1.0 M solution,

$$= \frac{1.0}{1000} \times 40.05 = 40.05 \times 10^{-3} \text{ mol}$$

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Now 2 mol of Ce^{4+} will oxidise n mole of Sn^{2+}

40.05×10^{-3} mol of Ce^{4+} will oxidise Sn^{2+}

$$= \frac{n}{2} \times 40.05 \times 10^{-3} \text{ mol} = 20.02\, n \times 10^{-3} \text{ mol}$$

But moles of Sn^{2+} in 20.0 mL of 1.0 M solution

$$= \frac{1.0}{1000} \times 20.0 = 20.0 \times 10^{-3} \text{ mol}$$

$\therefore$ $20.02\, n \times 10^{-3}$ mol $= 20.0 \times 10^{-3}$ mol

$\therefore$ $n = 1$

Hence 1 mol of electrons are required in the reduction of each mol of Ce^{4+} ion.

$\therefore$ $Ce^{4+} + e^- \longrightarrow Ce^{3+}$

Ce^{3+} is the reduction product.

Q.12. 3.90×10^{-3} moles of a solution containing an ion A^{n+} require 2.34×10^{-3} moles of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acidic medium. What is the value of n ?

Ans. Oxidation and reduction reactions are :

Reduction :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad ...(i)$$

Oxidation :

$$A^{n+} + 3H_2O \longrightarrow AO_3^- + 6H^+ + (5-n)e^- \quad ...(ii)$$

In a redox reaction, no. of electrons lost must be equal to no. of electrons gained, therefore, multiply eq. (i) by $(5–n)$ and eq(ii) by 5 so that

$$(5-n)\, MnO_4^- = 5A^{n+}$$

$\therefore$ $(5-n)$ moles of MnO_4^- will oxidise 5 moles of A^{n+}

or 2.34×10^{-3} moles of MnO_4^- will oxidise A^{n+}

$$= \frac{5}{5-n} \times 2.34 \times 10^{-3} \text{ moles}$$

But number of moles of A^{n+} actually oxidised $= 3.90 \times 10^{-3}$ moles

$\therefore$ $\frac{5}{5-n} \times 2.34 \times 10^{-3} = 3.90 \times 10^{-3}$

or $5 \times 2.34 = (5-n) \times 3.90$

$11.70 = 19.5 - 3.90\, n$

or $3.90\, n = 19.5 - 11.7 = 7.8$

$$n = \frac{7.8}{3.9} = 2$$

$\therefore$ Value of $n = 2$

Q. 13. 15.0 mL of 0.05 M SeO_2 reacts with 30.6 mL of 0.1 M $CrSO_4$ solution. If during the reaction $CrSO_4$ gets oxidised to $Cr_2(SO_4)_3$, to what oxidation state does selenium get converted ?

Ans. Moles of Se^{4+} ions present in 15.0 mL of 0.05

$$M = \frac{0.05}{1000} \times 15.0 = 7.5 \times 10^{-4} \text{ mole}$$

Moles of Cr^{2+} ions present in 30.6 mL of 0.1 M solution

$$= \frac{0.1}{1000} \times 30.6 = 3.06 \times 10^{-3} \text{ mole}$$

The oxidation reduction reactions are :

$$Cr^{2+} \longrightarrow Cr^{3+} + e^- \quad ...(i)$$

$$Se^{4+} + ne^- \longrightarrow Se^{(4-n)+} \quad ...(ii)$$

Multiply eqn. (i) by n and add to eqn. (ii)

$$nCr^{2+} + Se^{4+} \longrightarrow 4Cr^{3+} + Se^{(4-n)+}$$

According to the reaction

n mole of Cr^{2+} will reduce 1 mole of Se^{4+}

3.06×10^{-3} mole of Cr^{2+} will reduce Se^{4+}

$$= \frac{1}{n} \times 3.06 \times 10^{-3} \text{ mole}$$

But Se^{4+} actually reduced $= 7.5 \times 10^{-4}$ mole

$\therefore$ $\frac{3.06 \times 10^{-3}}{n} = 7.5 \times 10^{-4}$

or $n = \frac{3.06 \times 10^{-3}}{7.5 \times 10^{-4}} = 4$

$\therefore$ Reduction of 1 mole SeO_2 requires 4 electrons. Hence, Se^{4+} is reduced to Se^0.

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Define oxidant and reductant.
2. Define oxidation and reduction.
3. What is the oxidation number of Mn in MnO_2 ?
4. In the following reaction, predict the oxidising agent and reducing agent

$$Cr_2O_7^{2-} + 6\, Fe^{2+} + 14\, H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

5. What is the average oxidation number of carbon in acetone (CH_3COCH_3) ?
6. Can oxidation number be zero ? Illustrate.
7. Will oxidation number increase or decrease in a reduction reaction ?
8. What is the oxidation number of oxygen in H_2O_2 ?
9. Calculate the oxidation number of lead in Pb_3O_4.
10. Identify the oxidising and reducing agent in the following reaction :

$$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 2H_2O$$

11. Give an example of a compound in which the oxidation number is fractional.
12. Calculate the oxidation number of phosphorous in $Mg_2P_2O_7$.
13. Indicate the oxidizing and reducing agents in the following reaction :

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$$

14. Calculate the oxidation number of N in NO_3^-.
15. The oxidation number of B in $Na_2\, B_4O_7$ is +3. Is the statement correct ?
16. What is the oxidation number of Cr in CrO_2Cl_2 ?
17. Calculate the oxidation number of C in $C_6H_{12}O_6$.

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18. Identify oxidant and reductant in the following reaction :

$I_2\,(aq) + 2S_2O_3^{2-}\,(aq) \longrightarrow 2I^-\,(aq) + S_4O_6^{2-}$

19. In the reaction :

$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$, which species is oxidized ?

20. Name a compound each in which the oxidation state of O is (*i*) +2 and (*ii*) –2.

21. Name the type of reactions that occur at cathode in an electrochemical cell. Give one example.

22. The reduction potentials are :

$Cl_2 + 2e^- = 2\,Cl^-$ $\quad E^\circ = 1.36$ V

$F_2 + 2e^- = 2\,F^-$ $\quad E^\circ = 2.87$ V

Which is a better oxidising agent ?

23. What is the oxidation number of S in the reactants and the products :

$2\,Na_2\,S_2\,O_3 + I_2 \longrightarrow \quad Na_2S_4O_6 + 2NaI$

24. Can we store 1 M $AgNO_3$ in a copper vessel ? Given

$E^\circ_{Cu^{2+}|\,Cu} = +\,0.34$ V, $E^\circ_{Ag^+|\,Ag} = +\,0.80$ V

Short Answer Questions *carrying 2 or 3 marks*

1. Define the terms : oxidation, reduction, oxidising agent and reducing agent according to electronic concept.

2. Comment on the statement : oxidation and reduction go side by side.

3. Which of the following reactions is oxidation and which is reduction ?

(*i*) $2H_2O + 2\,e^- \longrightarrow 2OH^- + H_2$

(*ii*) $Al \longrightarrow Al^{3+} + 3e^-$

(*iii*) $Fe^{3+} \longrightarrow Fe^{2+} - e^-$

(*iv*) $2O^{2-} + C \longrightarrow CO_2 + 4e^-$

(*v*) $Br^- \longrightarrow 1/2\,Br_2 + e^-$

(*vi*) $2H_2O - 4e^- \longrightarrow 4H^+ + O_2$

4. In the following reactions, explain which reactant is oxidised and which is reduced. Give reasons for your answer :

(*i*) $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$

(*ii*) $MnO_2 + 4HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

(*iii*) $2KI + Cl_2 \longrightarrow 2KCl + I_2$

(*iv*) $CuO + CO \longrightarrow CO_2 + Cu$

5. Calculate the oxidation number of :

(*i*) S in $Na_2S_2O_3$ (*ii*) Cl in $HClO_4$

(*iii*) Mn in MnO_2 (*iv*) Boron in $Na_2B_4O_7$

(*v*) Cr in $K_2Cr_2O_7$

6. What is the oxidation number of S in the following :

(*i*) SO_2 (*ii*) Na_2S_2 (*iii*) S^{2-}

(*iv*) CS_2 (*v*) S_2Cl_2

7. What is the oxidation number of hydrogen in the following:

(*i*) H^+ (*ii*) NaH (*iii*) H_2 (*iv*) $LiAlH_4$

8. Calculate the oxidation number of underlined atom in the following :

(*i*) $Na\underline{Au}Cl_4$ (*ii*) $\underline{O}F_2$ (*iii*) $Ca(\underline{Cl}O_2)_2$

(*iv*) $\underline{N}H_2OH$ (*v*) $\underline{Se}O_3^{2-}$

9. State the maximum and minimum oxidation state of each of the following :

(*i*) Ta (*ii*) V (*iii*) S (*iv*) N

10. Calculate the oxidation number of the underlined atom :

(*i*) K $\underline{Mn}\,O_4$ (*ii*) $\underline{P}_2O_5$ (*iii*) $\underline{Fe}_2\,O_3$ (*iv*) $\underline{Xe}\,OF_4$

(*v*) $\underline{S}_2\,O_3^{2-}$ (*vi*) $\underline{Cr}_2\,O_7^{2-}$.

11. In the following reactions, label the oxidising agent and the reducing agent :

(*a*) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

(*b*) $PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$

(*c*) $2Al + 3F_2(g) \longrightarrow 2AlF_3(s)$.

12. How will you differentiate between oxidation number and valency ?

13. Arrange the following in the decreasing order of oxidation number of Mn :

(*i*) $KMnO_4$ (*ii*) MnO_2 (*iii*) Mn_2O_3

(*iv*) Mn (*v*) K_2MnO_4

14. Define oxidation and reduction according to electronic concept. Comment "oxidation and reduction always go side by side".

15. Balance the following redox reaction by oxidation number method :

$Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$ (basic medium)

16. Consider the reaction :

$2HBr + Cl_2 \longrightarrow 2HCl + Br_2$

Identify the substance

(*i*) getting reduced (*ii*) getting oxidised

(*iii*) acting as reducing agent

(*iv*) acting as oxidising agent.

Long Answer Questions *carrying 5 marks*

1. Balance the following equations using oxidation number method :

(*i*) $MnO_4^- + H^+ + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

(*ii*) $Zn + NO_3^- + H^+ \longrightarrow Zn^{2+} + H_2O$

(*iii*) $H_2SO_3 + I_2 + H_2O \longrightarrow H_2SO_4 + HI$

(*iv*) $HNO_3 + I_2 \longrightarrow HIO_3 + NO_2 + H_2O$

(*v*) $MnO_4^- + H_2O_2 \longrightarrow MnO_4^{2-} + O_2$

(in alkaline medium)

2. Balance the following equations by oxidation number method :

(*i*) $H_2S + HNO_3 \longrightarrow H_2O + NO + S$

(*ii*) $NH_3 + O_3 \longrightarrow NO + H_2O$

(*iii*) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$.

3. Balance the following equations by ion electron (half reaction) method :

(*i*) $H_2S + MnO_4^- + H^+ \longrightarrow S + Mn^{2+} + H_2O$

(*ii*) $Cr_2O_7^{2-} + H^+ + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(*iii*) $AsO_3^{3-} + IO_3^- \longrightarrow AsO_4^{3-} + I^-$

(*iv*) $SnO_2 + C \longrightarrow Sn + CO$.

4. What are redox reactions ? Discuss with examples. Give important applications of redox reactions.

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5. Write short notes on :

(a) Electrochemical series

(b) Redox titrations

(c) Abnormal oxidation number and structures of compounds.

6. Identify the redox reactions out of the following reactions and identify the oxidising and reducing agents in them.

(i) $3HCl(aq) + HNO_3\,(aq) \longrightarrow Cl_2\,(g) + NOCl\,(g) + 2H_2O\,(l)$

(ii) $HgCl_2\,(aq) + 2KI\,(aq) \longrightarrow HgI_2\,(s) + 2KCl\,(aq)$

(iii) $Fe_2O_3\,(s) + 3CO\,(g) \xrightarrow{\Delta} 2Fe\,(s) + 3CO_2\,(g)$

(iv) $PCl_3\,(l) + 3H_2O\,(l) \longrightarrow 3HCl\,(aq) + H_3PO_3\,(aq)$

(v) $4NH_3 + 3O_2\,(g) \longrightarrow 2N_2\,(g) + 6H_2O\,(g)$

7. Write balanced chemical equation for the following reactions :

(i) Permanganate ion (MnO_4^-) reacts with sulphur dioxide gas in acidic medium to produce Mn^{2+} and hydrogen sulphate ion.

(Balance by ion electron method)

(ii) Reaction of liquid hydrazine (N_2H_4) with chlorate ion (ClO_3^-) in basic medium produces nitric oxide gas and chloride ion in gaseous state.

(Balance by oxidation number method)

(iii) Dichlorine heptaoxide (Cl_2O_7) in gaseous state combines with an aqueous solution of hydrogen peroxide in acidic medium to give chlorite ion (ClO_2^-) and oxygen gas.

(Balance by ion electron method)

8. Balance the following equations by the oxidation number method.

(i) $Fe^{2+} + H^+ + Cr_2O_7^{2-} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(ii) $I_2 + NO_3^- \longrightarrow NO_2 + IO_3^-$

(iii) $I_2 + S_2O_3^{2-} \longrightarrow I^- + S_4O_6^{2-}$

(iv) $MnO_2 + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$

Hints & Answers for Revision Exercises

Very Short Answer Questions

3. + 4 **5.** 4/3 **6.** Yes **7.** decrease

8. – 1 **9.** + 8/3 **11.** $Na_2S_4O_6$ **12.** + 5

13. Cu^{2+} : Oxidizing agent, I^- : reducing agent

14. + 5. **15.** Correct **16.** + 6

Short Answer Questions

3. Reduction reaction (i), (iii) and oxidation reaction (ii), (iv), (v), (vi)

4. (i) SO_2 is reduced and H_2S is oxidised.
(ii) MnO_2 is reduced and HCl is oxidised.
(iii) Cl_2 is reduced and KI is oxidised.
(iv) CuO is reduced and C is oxidised.

5. (i) +2 (ii) +7 (iii) +4 (iv) +3 (v) +6

10. (i) +7 (ii) +5 (iii) +3 (iv) +6 (v) +2 (vi) +6

13. $KMnO_4$, K_2MnO_4, MnO_2, Mn_2O_3, Mn

Long Answer Questions

1. (i) $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^2 + 5Fe^{3+} + 4H_2O$

(ii) $4Zn + NO_3^- + 10H^+ \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

(iii) $H_2SO_3 + I_2 + H_2O \longrightarrow H_2SO_4 + 2HI$

(iv) $10HNO_3 + I_2 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(v) $2MnO_4^- + 2OH^- + H_2O_2 \longrightarrow 2MnO_4^{2-} + O_2 + 2H_2O$

2. (i) $3H_2S + 2HNO_3 \longrightarrow 2NO + 3S + 4H_2O$

(ii) $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$

(iii) $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

3. (i) $5H_2S + 2MnO_4^- + 16H^+ \longrightarrow 5S + 2Mn^{2+} + 8H_2O$

(ii) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(iii) $3AsO_3^{3-} + IO_3^- \longrightarrow 3AsO_4^{3-} + I^-$

(iv) $SnO_2 + 2C \longrightarrow Sn + 2CO$

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OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the correct answer :

Oxidation, Reduction and Oxidation Number

A1. Reduction involves :
(*a*) gain of electrons
(*b*) addition of oxygen
(*c*) increase in oxidation number
(*d*) loss of electrons.

A2. Oxidation number of P in PO_4^{3-} ion is :
(*a*) – 3 (*b*) + 7
(*c*) + 5 (*d*) + 3.

A3. Oxidation number of Mn in MnO_4^- ion is :
(*a*) +1 (*b*) –7
(*c*) –1 (*d*) +7.

A4. Oxidation number of C in CH_3OH, CH_2O, HCOOH and C_2H_2 is respectively :
(*a*) –2, 0, +2, –1 (*b*) +2, 0, +2, –2
(*c*) –2, 0, +2, 0 (*d*) –2, –4, +2, –2

A5. What is the oxidation state of S in Na_2S_2 ?
(*a*) +1 (*b*) –2
(*c*) –1 (*d*) 0.

A6. The oxidation state of S in Caro's acid (permono sulphuric acid) H_2SO_5 is
(*a*) +8 (*b*) +6
(*c*) +5 (*d*) +4

A7. Oxidation number of sodium in sodium amalgam (Na/Hg) is
(*a*) 0 (*b*) +1
(*c*) –1 (*d*) +2

A8. In the reaction : $Cl_2 + 2OH^- \longrightarrow OCl^- + Cl^- + H_2O$
(*a*) OH^- is oxidising and Cl^- is reducing agent
(*b*) Cl_2 is oxidising and OH^- is reducing agent
(*c*) OH^- is both oxidising and reducing agent
(*d*) Cl_2 is both oxidising and reducing agent.

A9. The oxidation state of S in $S_2O_8^{2-}$ is
(*a*) +2 (*b*) +4
(*c*) +6 (*d*) +7

A10. In which of the following compounds, the oxidation number of carbon is not zero ?
(*a*) $C_{12}H_{22}O_{11}$ (*b*) HCHO
(*c*) CH_3CHO (*d*) CH_3COOH.

A11. The oxidation states of V and Br in $V(BrO_2)_2$ are respectively
(*a*) 2 and 2 (*b*) 2 and 1
(*c*) 4 and 2 (*d*) 2 and 3.

A12. The oxidation state of N in HN_3 is
(*a*) +3 (*b*) –3 (*c*) –1/3 (*d*) +1/3

A13. In which of the following S has highest oxidation state?
(*a*) $Na_2S_4O_6$ (*b*) S_2Cl_2
(*c*) S_8 (*d*) H_2SO_4

A14. Which of the following rules for oxidation number is not correct ?
(*a*) The algebraic sum of all the oxidation numbers in a compound is zero.
(*b*) An element in the free or the uncombined state bears oxidation number zero.
(*c*) The oxidation number of hydrogen is always +1.
(*d*) In all its compounds, the oxidation number of fluorine is –1.

A15. In the reaction :
$3CuO + 2NH_3 \longrightarrow N_2 + 3H_2O + 3Cu$
the change of NH_3 to N_2 involve
(*a*) Loss of 6 electrons per mol of N_2
(*b*) Loss of 3 electrons per mol of N_2
(*c*) Gain of 6 electrons per mol of N_2
(*d*) Gain of 3 electrons per mol of N_2

A16. Which of the following statement is not correct ?
(*a*) Oxidant is a substance which increases the oxidation number of other substance.
(*b*) Reductant is a substance which decreases the oxidation number of other substance.
(*c*) The oxidation number of oxidant decreases.
(*d*) In oxidation there is decrease in oxidation number.

A17. When phosphorus reacts with caustic soda, the products are PH_3 and NaH_2PO_2. The reaction is an example of
(*a*) oxidation (*b*) reduction
(*c*) disproportionation (*d*) none of these.

A18. Which of the following is not an example of redox reaction ?
(*a*) $CuO + H_2 \longrightarrow Cu + H_2O$
(*b*) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
(*c*) $2K + F_2 \longrightarrow 2KF$
(*d*) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$

Answers

A1. (*a*) **A2.** (*c*) **A3.** (*d*) **A4.** (*a*) **A5.** (*c*) **A6.** (*b*) **A7.** (*a*) **A8.** (*d*) **A9.** (*c*) **A10.** (*c*)
A11. (*d*) **A12.** (*c*) **A13.** (*d*) **A14.** (*c*) **A15.** (*a*) **A16.** (*d*) **A17.** (*c*) **A18.** (*d*)

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A19. The oxidation state of Cr in $Cr(CO)_6$ is
(a) 0 (b) +2
(c) –2 (d) +6.

A20. The oxidation state of oxygen in H_2O_2 is
(a) –1 (b) +2
(c) –2 (d) +1.

A21. The oxidation state of phosphorus in $Ba(H_2PO_2)_2$ is
(a) +3 (b) +2
(c) +1 (d) –1

A22. The oxidation number of S in S_8, S_2F_2 and H_2S respectively are :
(a) 0, +1, –2 (b) +2, +1, –2
(c) 0, +1, +2 (d) +2, +1, –2

A23. In the reaction :
$3Br_2 + 6CO_3^{2-} + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6HCO_3^-$
(a) Br_2 is oxidised and carbonate is reduced.
(b) Bromine is reduced and water is oxidised.
(c) Bromine is neither reduced nor oxidised
(d) Bromine is both reduced and oxidised.

A24. Oxidation state of Fe in Fe_3O_4 is
(a) +2 (b) +3
(c) +8/3 (d) +2/3

A25. In Br_3O_8 compound, oxidation number of bromine is
(a) 16/13 (b) 26/3
(c) 24/3 (d) 16/3

A26. Which is the best description of the behaviour of bromine in the reaction
$H_2O + Br_2 \longrightarrow HOBr + HBr$
(a) Proton acceptor only
(b) Both oxidised and reduced
(c) Oxidised only
(d) Reduced only

A27. The oxidation number of H in $LiAlH_4$ is
(a) –1 (b) +1 (c) 0 (d) +3

A28. The oxidation states of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order :
(a) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$
(b) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$
(c) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$
(d) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$

Balancing Redox Reactions and Electrochemical Cells

A29. E°values of some redox couples are given below. On the basis of these values choose the correct option.
E°values : $Br_2 | Br^- = +1.90$; $Ag^+ | Ag(s) = +0.80$
$Cu^{2+} | Cu(s) = +0.34$; $I_2(s) | I^- = +0.54$
(a) Cu will reduce Br^- (b) Cu will reduce Ag
(c) Cu will reduce I^- (d) Cu will reduce Br_2

A30. On the basis of standard electrode potential of redox couples given below find out which of the following is the strongest oxidising agent.
E°values : $Fe^{3+} | Fe^{2+} = +0.77$; $I_2(s) | I^- = +0.54$;
$Cu^{2+} | Cu = +0.34$; $Ag^+ | Ag = +0.80$V
(a) Fe^{3+} (b) $I_2(s)$
(c) Cu^{2+} (d) Ag^+

A31. The coefficients x, y and z in the following balanced equation :
$x\,Zn + y NO_3^- \longrightarrow z Zn^{2+} + NH_4^+$ (in basic medium) are
(a) 4, 1, 4 (b) 2, 2, 2
(c) 4, 2, 4 (d) 4, 4, 4

A32. The following four colourless salt solutions are placed in separate test tubes and a strip of a copper is placed in each. Which of the following solutions will finally turn blue ?
(a) NaCl (b) $AgNO_3$
(c) $ZnSO_4$ (d) $Cd(NO_3)_2$.

A33. In a standard hydrogen electrode, the concentration of H^+ is :
(a) 0.1 M (b) 1 M
(c) 10 M (d) Not fixed.

A34. In a galvanic cell, which of the following statement is correct ?
(a) anode is negatively charged
(b) cathode is positively charged
(c) reduction occurs at anode
(d) standard e.m.f of the cells is always zero.

A35. For the redox reaction :
$MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$
The correct coefficients of the reactants in the balanced reaction are :

MnO_4^-	Fe^{2+}	H^+
(a) 1	5	8
(b) 2	5	8
(c) 4	5	16
(d) 2	5	16

A36. The standard reduction potential values of the three metallic cations X, Y and Z are 0.52, –3.03 and –1.18 V respectively. The order of reducing power of the corresponding metal is ?
(a) Y > Z > X (b) X > Y > Z
(c) Z > Y > X (d) Z > X > Y

A37. A gas at 1 atm is bubbled through a solution containing 1M Y^- and 1 M Z^- at 25° C. If the reduction potential of Z > Y > Z, then
(a) Y will oxidize X and not Z
(b) Y will oxidise Z and not X
(c) Y will oxidize both X and Z
(d) Y will reduce both X and Z.

Answers

A19. (a) **A20.** (a) **A21.** (c) **A22.** (a) **A23.** (d) **A24.** (c) **A25.** (d) **A26.** (b) **A27.** (a) **A28.** (a)
A29. (d) **A30.** (d) **A31.** (a) **A32.** (b) **A33.** (b) **A34.** (c) **A35.** (a) **A36.** (a) **A37.** (a)

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A38. Standard electrode potentials are :
$Fe^{2+} | Fe$ ($E^\circ = -0.44$ V), $Fe^{3+} | Fe^{2+}$ ($E^\circ = 0.77$ V)
Fe^{2+}, Fe^{3+} and Fe blocks are kept together, then
(*a*) Fe^{3+} increases
(*b*) Fe^{3+} decreases
(*c*) Fe^{2+}/Fe^{3+} remains unchanged
(*d*) Fe^{2+} decreases

A39. For decolourization of 1 mole of $KMnO_4$, the moles of H_2O_2 required is
(*a*) 1/2 (*b*) 3/2
(*c*) 5/2 (*d*) 7/2

Answers

38. (*b*) **39.** (*c*)

B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

AIPMT & Other State Boards' Medical Entrance

B1. Which of the following is a redox reaction ?
(*a*) $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$
(*b*) $SO_2 + H_2O \longrightarrow H_2SO_3$
(*c*) $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$
(*d*) $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$
(*e*) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
(Kerala P.M.T. 2007)

B2. Oxidation number of iodine in IO^-_3, IO^-_4, KI and I_2 respectively are
(*a*) –1, –1, 0, +1 (*b*) +3, +5, +7, 0
(*c*) +5, +7, –1, 0 (*d*) –1, –5, –1, 0
(*e*) –2, –5, –1, 0 *(Kerala PMT 2008)*

B3. In the balanced chemical equation,
$IO_3^- + aI^- + bH^+ \longrightarrow cH_2O + dI_2$
a, *b*, *c* and *d* respectively correspond to
(*a*) 5, 6, 3, 3 (*b*) 5, 3, 6, 3
(*c*) 3, 5, 3, 6 (*d*) 5, 6, 5, 5
(AFMC 2009)

B4. Number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acidic medium will be :
(*a*) 0.6 moles (*b*) 0.4 moles
(*c*) 7.5 moles (*d*) 0.2 moles
(CBSE Med. 2008)

B5. On the basis of following E° values, the strongest oxidising agent is
$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e^-$ $E^\circ = -0.35$ V
$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $E^\circ = -0.77$ V
(*a*) $[Fe(CN)_6]^{4-}$ (*b*) Fe^{2+}
(*c*) Fe^{3+} (*d*) $[Fe(CN)_6]^{3-}$
(CBSE Med 2008)

B6. In the redox reaction
$xKMnO_4 + NH_3 \longrightarrow yKNO_3 + MnO_2 + KOH + H_2O$
(*a*) $x = 4, y = 6$ (*b*) $x = 8, y = 6$
(*c*) $x = 3, y = 8$ (*d*) $x = 8, y = 3$
(DUMET 2009)

B7. Which of the following have been arranged in decreasing order of oxidation number of sulphur ?
(*a*) $Na_2S_4O_6 > H_2S_2O_7 > Na_2S_2O_3 > S_8$
(*b*) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$
(*c*) $SO_2^{2+} > SO_4^{2-} > SO_3^{2-} > HSO_4^-$
(*d*) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$
(A.M.U. Med 2010)

B8. The average oxidation state of sulphur in $Na_2S_4O_6$ is
(*a*) + 2.5 (*b*) + 2
(*c*) + 3.0 (*d*) + 3.5
(*e*) + 4 *(Kerala PMT 2010)*

B9. Standard electrode potential of three metals X, Y and Z are – 1.2 V, +0.5 V and – 3.0 V respectively. The reducing power of these metals will be
(*a*) Y > Z > X (*b*) Y > X > Z
(*c*) Z > X > Y (*d*) X > Y > Z *(A.I.P.M.T. 2011)*

B10. In which of the following compounds, nitrogen exhibits highest oxidation state ?
(*a*) N_2H_4 (*b*) NH_3
(*c*) N_3H (*d*) NH_3OH *(A.I.P.M.T. 2012)*

B11. A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. During the reaction which element undergoes maximum change in the oxidation number ?
(*a*) S (*b*) H
(*c*) Cl (*d*) C *(A.I.P.M.T. 2012)*

B12. In acidic medium, H_2O_2 changes $Cr_2O_7^{2-}$ to CrO_5 which has two (—O—O—) bonds. Oxidation state of Cr in CrO_5 is
(*a*) +5 (*b*) +3
(*c*) +6 (*d*) –10 *(A.I.P.M.T. 2014)*

Answers

B1. (*a*) **B2.** (*c*) **B3.** (*a*) **B4.** (*a*) **B5.** (*c*) **B6.** (*d*) **B7.** (*d*) **B8.** (*a*) **B9.** (*c*) **B10.** (*c*) **B11.** (*c*) **B12.** (*c*)

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B13. Choose the disproportionation reaction among the following redox reactions.

(a) $3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$

(b) $P_4(s) + 3NaOH(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3NaH_2PO_2(aq)$

(c) $Cl_2(g) + 2KI(aq) \longrightarrow 2KCl(aq) + I_2(s)$

(d) $Cr_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Cr(s)$

(e) $2NaH(s) \longrightarrow 2Na(s) + H_2(g)$ *(Kerala P.M.T. 2015)*

B14. Which of the following processes does not involve oxidation of iron?

(a) Formation of $Fe(CO)_5$ from Fe

(b) Liberation of H_2 from steam by iron at high temperature.

(c) Rusting of iron sheets.

(d) Decolourisation of blue $CuSO_4$ solution by iron *(A.I.P.M.T. 2015)*

B15. Assuming complete ionization, same moles of which of the following compounds will require the least amount of acidified $KMnO_4$ for complete oxidation?

(a) FeC_2O_4 (b) $Fe(NO_2)_2$

(c) $FeSO_4$ (d) $FeSO_3$ *(A.I.P.M.T. 2015)*

B16. For the redox reaction

$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$

The correct coefficients of the reactants for the balanced equation are

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	16	5	2
(b)	2	5	16
(c)	2	16	5
(d)	5	16	2

(NEET 2018)

JEE (Mains) & Other State Boards' Engineering Entrance

B17. When $KMnO_4$ acts as an oxidising agent and ultimately forms MnO_4^{2-}, MnO_2, Mn_2O_3 and Mn^{2+}, then the number of electrons transferred in each case is

(a) 4, 3, 1, 5 (b) 1, 5, 3, 7

(c) 1, 3, 4, 5 (d) 3, 5, 7, 1 *(A.I.E.E.E.2002)*

B18. $aK_2Cr_2O_7 + bKCl + cH_2SO_4 \longrightarrow xCrO_2Cl_2 + yKHSO_4 + 3H_2O$

The above equation balances when

(a) $a = 2, b = 4, c = 6$ and $x = 2, y = 6, z = 3$

(b) $a = 4, b = 2, c = 6$ and $x = 6, y = 2, z = 3$

(c) $a = 6, b = 4, c = 2$ and $x = 6, y = 3, z = 2$

(d) $a = 1, b = 4, c = 6$ and $x = 2, y = 6, z = 3$

(e) $a = 1, b = 6, c = 4$ and $x = 6, y = 2, z = 3$ *(Kerala P.E.T.2004)*

B19. Consider the following E° values

$E°(Fe^{3+} | Fe^{2+}) = +0.77\ V$; $E°(Sn^{2+} | Sn) = -0.14\ V$

Under standard conditions, the potential for the reaction:

$Sn(s) + 2Fe^{3+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$ is

(a) 0.19 V (b) 0.140 V

(c) 1.68 V (d) 0.63 V *(A.I.E.E.E. 2004)*

B20. In a cell that utilizes the reaction :

$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

addition of H_2SO_4 to cathode compartment will

(a) increase the E and shift equilibrium to the right

(b) lower the E and shift equilibrium to the left

(c) lower the E and shift equilibrium to the left

(d) increase the E and shift equilibrium to the left *(A.I.E.E.E. 2004)*

B21. $a\ K_2Cr_2O_7 + b\ KCl + c\ H_2SO_4 \longrightarrow x\ CrO_2Cl_2 + y\ KHSO_4 + zH_2O$

The above equation balances when

(a) $a = 2, b = 4, c = 6$ and $x = 2, y = 6, z = 3$

(b) $a = 4, b = 2, c = 6$ and $x = 6, y = 2, z = 3$

(c) $a = 6, b = 4, c = 2$ and $x = 6, y = 3, z = 2$

(d) $a = 1, b = 4, c = 6$ and $x = 2, y = 6, z = 3$

(e) $a = 1, b = 6, c = 4$ and $x = 6, y = 2, z = 3$ *(Kerala P.E.T. 2004)*

B22. What products are expected from the disproportionation reaction of hypochlorous acid ?

(a) HClO and $HClO_4$

(b) HCl and Cl_2O

(c) HCl and $HClO_3$

(d) $HClO_3$ and Cl_2O *(A.I.E.E.E. 2006)*

B23. What is the oxidation number of carbonyl carbon in methanal ?

(a) +3 (b) +2

(c) +4 (d) 0 *(Gujarat C.E.T. 2007)*

B24. The standard oxidation potentials of Zn, Cu, Ag and Ni electrodes are +0.76, –0.34, –0.80 and +0.25 V respectively. Which of the following reaction will provide maximum voltage ?

(a) $Cu + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag$

(b) $Zn + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag$

(c) $H_2 + Ni^{2+}(aq) \longrightarrow 2H^+(aq) + Ni$

(d) $Zn + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu$

(e) $Zn + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2$ *(Kerala C.E.T. 2007)*

Answers

B13. (b) **B14.** (a) **B15.** (c) **B16.** (b) **B17.** (c) **B18.** (d) **B19.** (a) **B20.** (a) **B21.** (d) **B22.** (c) **B23.** (d) **B24.** (b)

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B25. Oxidation number of Mn atom in $KMnO_4$ is
(a) 6 (b) 7
(c) 14 (d) 5 *(B.H.U. 2007)*

B26. When sulphur dioxide is passed in an acidified $K_2Cr_2O_7$ solution, the oxidation state of sulphur is changed from
(a) +4 to +6 (b) +6 to +4
(c) +4 to 0 (d) +4 to +2
(Karnataka C.E.T. 2008)

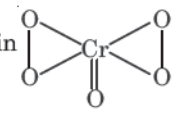
B27. Hydrogen gas is not liberated when the following metal is added to dil. HCl
(a) Mg (b) Sn
(c) Ag (d) Zn *(Karnataka C.E.T. 2008)*

B28. Which one of the following reactions involves disproportionation?
(a) $2H_2SO_4 + Cu \longrightarrow CuSO_4 + 2H_2O + SO_2$
(b) $As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$
(c) $2KOH + Cl_2 \longrightarrow KCl + KOCl + H_2O$
(d) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
(e) $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$ *(Kerala PET 2008)*

B29. In which of the following the oxidation number of oxygen has been arranged in increasing order?
(a) $OF_2 < KO_2 < BaO_2 < O_3$
(b) $BaO_2 < KO_2 < O_3 < OF_2$
(c) $BaO_2 < O_3 < OF_2 < KO_2$
(d) $KO_2 < OF_2 < O_3 < BaO_2$
(e) $OF_2 < O_3 < KO_2 < BaO_2$ *(Kerala PET 2008)*

B30. Electrode potential of hydrogen electrode is ... volt
(a) 0 (b) +1
(c) –1 (d) None of these
(Orissa JEE 2008)

B31. The reaction
$P_4 + 3\,NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$
is an example of
(a) Disproportionation reaction
(b) Neutralisation reaction
(c) Double decomposition reaction
(d) Pyrolytic reaction *(Orissa JEE 2008)*

B32. Oxidation state of chromium in  is
(a) +10 (b) +6
(c) +3 (d) +2 *(Orissa JEE 2008)*

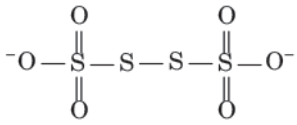
B33. The oxidation number of Fe in brown ring $[Fe(H_2O)_5NO]^{2+}$ is
(a) 0 (b) +1
(c) +2 (d) +3 *(Orissa JEE 2008)*

B34. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory results when carried out in the presence of HCl because HCl
(a) oxidises oxalic acid to carbon dioxide and water
(b) gets oxidised by oxalic acid to chlorine
(c) furnishes H^+ ions in addition to those from oxalic acid.
(d) reduces permanganate to Mn^{2+} *(AIEEE 2008)*

B35. The oxidation number of sulphur atoms in peroxomonosulphuric acid (H_2SO_5) and peroxodisulphuric acid ($H_2S_2O_8$) are respectively
(a) +8 and +7 (b) +3 and +3
(c) +6 and +6 (d) +4 and +4 *(J & K 2009)*

B36. Oxidation states of Fe in Mohr's salt is
(a) +1 (b) +2
(c) +3 (d) +4 *(Orissa-JEE 2009)*

B37. Oxidation state of S in $S_4O_6^{2-}$ from left to right are



(a) +6, 0, 0, +6 (b) +5, 0, 0, +5
(c) +3, +1, +1, +3 (d) +4, +1, +1, +4
(Orissa-JEE 2009)

B38. Oxidation number of P in PO_4^{3-}, S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$ are respectively
(a) +3, +6 and +5 (b) –3, +6 and +6
(c) +5, +3 and +6 (d) +5, +6 and +6
(Orissa-JEE 2009)

B39. The oxidation state of S in H_2SO_4 is
(a) + 2 (b) + 4
(c) + 6 (d) + 7 *(Orissa JEE 2010)*

B40. In chromite ore, the oxidation number of iron, and chromium are respectively
(a) + 3, + 2 (b) + 3, + 6
(c) + 2, + 6 (d) + 2, + 3
(Karnataka CET 2010)

B41. Which of the following species can function both as oxidizing as well as reducing agent ?
(a) Cl^- (b) ClO_4^-
(c) ClO^- (d) MnO_4^-
(e) NO_3^- *(Kerala PET 2010)*

Answers

B25. (b) **B26.** (a) **B27.** (c) **B28.** (c) **B29.** (b) **B30.** (a) **B31.** (a) **B32.** (b) **B33.** (b) **B34.** (d)
B35. (c) **B36.** (b) **B37.** (c) **B38.** (d) **B39.** (c) **B40.** (d) **B41.** (c)

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B42. If the molecular wt. of $Na_2S_2O_3$ and I_2 are M_1 and M_2 respectively, then what will be the equivalent wt. of $Na_2S_2O_3$ and I_2 in the following reaction ?

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

(a) M_1, M_2 (b) $M_1, M_2/2$
(c) $2M_1, M_2$ (d) $M_1, 2M_2$

(WB JEE 2011)

B43. In the reaction : $H_2S + H_2O_2 \longrightarrow S + 2H_2O$

(a) H_2S is an acid and H_2O_2 is a base.
(b) H_2S is a base and H_2O_2 is an acid.
(c) H_2S is an oxidising agent and H_2O_2 is a reducing agent
(d) H_2S is a reducing agent and H_2O_2 is oxidising agent.
(e) H_2S is hydrolysed to S.

(Kerala PET 2011)

B44. 1M solution each of $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is electrolysed using Pt-electrodes. The values of standard electrode potentials in volts are :

$Ag^+ | Ag = +0.80$ V, $Cu^{2+} | Cu = +0.34$V

$Hg_2^{2+} | Hg = +0.79$ V, $Mg^{2+} | Mg = -2.37$ V

The sequence of deposition of metals on the cathode will be

(a) Mg, Ag, Cu (b) Mg, Cu, Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag

(A.M.U. Engg. 2012)

B45. In the reaction,

$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$,

the oxidising agent is

(a) $FeSO_4$
(b) H_2SO_4
(c) H_2O_2
(d) both H_2SO_4 and H_2O_2

(Karnataka C.E.T. 2013)

B46. An electrochemical cell has two half cell reactions as:

$A^{2+} + 2e^- \longrightarrow A$; $E^0_{A^{2+}|A} = 0.34$ V

$X \longrightarrow X^{2+} + 2e^-$; $E^0_{X^{2+}|X} = -2.37$ V

The cell voltage will be

(a) 2.71 V (b) 2.03 V
(c) – 2.71 V (d) – 2.03 V

(J.K. C.E.T. 2013)

B47. Given

$E^0(Cr^{3+} | Cr) = -0.74$ V, $E^0(MnO_4^- | Mn^{2+}) = 1.51$ V

$E^0 Cr_2O_7^{2-} | Cr^{3+} = 1.33$ V, $E^0\ Cl | Cl^- = 1.36$ V

Based on the data given above, strongest oxidising agent will be

(a) Cl^- (b) Cr^{3+}
(c) Mn^{2+} (d) MnO_4^-

(JEE. Main 2013)

B48. Consider the following reaction :

$$x\,MnO_4^- + y\,C_2O_4^{2-} + zH^+ \longrightarrow x\,Mn^{2+} + 2y\,CO_2 + \frac{z}{2}\,H_2O$$

The values of x, y and z in the reaction are respectively

(a) 5, 2 and 16 (b) 2, 5 and 8
(c) 2, 5 and 16 (d) 5, 2 and 8

(JEE. Main 2013)

B49. In the redox reaction,

$$MnO_4^- + 8H^+ + 5Br^- \longrightarrow Mn^{2+} + 4H_2O + \frac{5}{2}Br_2$$

Which one is the reducing agent?

(a) H^+ (b) MnO_4^-
(c) Br^- (d) Mn^{2+}

(A.M.U. Engg. 2014)

B50. Potassium dichromate is a good oxidizing agent, in acidic medium. The oxidation state of chromium changes by

(a) 2 (b) 3
(c) 4 (d) 5

(M.H-C.E.T. 2015)

B51. One mole of hydrazine (N_2H_4) loses 10 moles of electrons in a reaction to form a new compound X. Assuming that all the nitrogen atoms in hydrazine appear in the new compound, what is the oxidation state of nitrogen in X?

(Note: There is no change in the oxidation state of hydrogen in the reaction).

(a) –1 (b) –3
(c) +3 (d) +5
(e) +1 *(Kerala PET 2016)*

Answers

B42. (b) **B43.** (d) **B44.** (c) **B45.** (c) **B46.** (a) **B47.** (d) **B48.** (c) **B49.** (c) **B50.** (b) **B51.** (c)

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B52. $3ClO^-(aq) \longrightarrow ClO_3^- + 2Cl^-$ is an example of
(a) oxidation reaction
(b) reduction reaction
(c) disproportionation reaction
(d) decomposition reaction *(Karnataka CET 2017)*

B53. How many electrons are involved during the oxidation reaction of $KMnO_4$ in acidic medium?
(a) 1 (b) 3
(c) 5 (d) 4
(J.K. CET 2018)

B54. For the redox reaction:
$xMnO_4^- + yH_2C_2O_4 + zH^+ \rightarrow mMn^{2+} + nCO_2 + pH_2O$.
The values of x, y, m and n are
(a) 10, 2, 5, 2 (b) 2, 5, 2, 10
(c) 6, 4, 2, 4 (d) 3, 5, 2, 10
(Karnataka CET 2018)

B55. Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y, is
(a) 7 (b) 1
(c) 5 (d) 3 *(JEE Main 2019)*

JEE (Advance) for IIT Entrance

B56. For the electrochemical cell $M \mid M^+ \parallel X^- \mid X$,
$E^0_{M^+|M} = 0.44$ V, $E^0_{X|X^-} = 0.33$ V
(a) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction
(b) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction
(c) $E^\circ_{cell} = 0.77$V.
(d) $E^\circ_{cell} = -0.77$V.
(I.I.T. 2000)

B57. Standard electrode potential data are used for understanding the stability of an oxidant in a redox titration. Some half reactions and their standard potentials are given below :

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$ $E^\circ = 1.51$ V

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E^\circ = 1.38$ V

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ $E^\circ = 0.77$ V

$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ $E^\circ = 1.40$ V

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$.
(a) MnO_4^- can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4
(I.I.T. 2002)

B58. The pairs of compounds having metals in their highest oxidation state is
(a) MnO_2, $FeCl_3$
(b) MnO_4^-, CrO_2Cl_2
(c) $[Fe(CN)_6]^{3-}$, $Co(CN)_3$
(d) $[NiCl_4]^{2-}$, $[CoCl_4]^-$
(I.I.T. 2004)

B59. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen ?
(a) HNO_3, NO, NH_4Cl,N_2
(b) HNO_3, NO, N_2, NH_4Cl
(c) HNO_3, NH_4Cl, NO, N_2
(d) NO, HNO_3, NH_4Cl, N_2 *(I.I.T. J.E.E. 2012)*

Answers

B52. (c) **B53.** (c) **B54.** (b) **B55.** (c) **B56.** (b) **B57.** (a) **B58.** (b) **B59.** (b)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Which of the following are redox reactions ?
(a) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$
(b) $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$
(c) $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$
(d) $KCN + AgCN \longrightarrow K[Ag(CN)_2]$

C2. In which of the following the oxidation number of atom is/are correctly given ?
(a) $C_6H_{12}O_6$: C = 0
(b) $Na_4[Fe(CN)_6]$: Fe = + 3
(c) HCOOH : C = + 4
(d) HCHO : C = 0

Answers

C1. (b, c) **C2.** (a, d)

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C3. Which of the following act both as an oxidising as well as reducing agent ?

(*a*) HNO_3 (*b*) H_2O_2 (*c*) HNO_2 (*d*) H_2S

C4. In which of the following the oxidation number of the underlined atom is maximum ?

(*a*) $H_4\underline{P}_2O_7$ (*b*) $K\underline{Al}(SO_4)_2.12H_2O$

(*c*) $K_2\underline{Mn}O_4$ (*d*) $Na_2\underline{S}O_3$

C5. Oxidation number of Cr in CrO_5 is same as of S in

(*a*) H_2SO_5 (*b*) $Na_2S_4O_6$ (*c*) $Na_2S_2O_7$ (*d*) H_2SO_3

C6. Which of the following statements are not correct for the following reaction :

$2MnO_4^- + 6I^- + 4H_2O \longrightarrow 2MnO_2 + 3I_2 + 8OH^-$

(*a*) Oxidation number of Mn in MnO_4^- and MnO_2 are same

(*b*) MnO_4^- acts as an oxidising agent

(*c*) H_2O has been reduced

(*d*) Oxidation number of iodide has increased from I^- to I_2.

C7. Which of the following statements are wrong ?

(*a*) Reduction involves gain of electrons.

(*b*) The oxidation number of reducing agent decreases.

(*c*) Oxidising agent helps to increase the oxidation number of reducing agent.

(*d*) Oxidation involves gain of electrons.

C8. Consider the redox reaction :

$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

(*a*) $2S_2O_3^{2-}$ gets oxidised to $S_4O_6^{2-}$

(*b*) I_2 gets oxidised to I^-

(*c*) there is increase in oxidation number of iodine during the reaction

(*d*) The total increase in oxidation number of sulphur is +1 during the reaction

C9. For the reaction:

$I^- + ClO_3^- + H_2SO_4 \longrightarrow Cl^- + HSO_4^- + I_2$

The correct statement(s) in the balanced equation is/are

(*a*) stoichiometric coefficient of HSO_4^- is 6

(*b*) iodide is oxidised

(*c*) sulphur is reduced

(*d*) H_2O is one of the products. *(JEE advance 2014)*

Answers

C3. (*b, c*) **C4.** (*b, c*) **C5.** (*a, c*) **C6.** (*b, d*) **C7.** (*b, d*) **C8.** (*a, d*) **C9.** (*a, b, d*)

D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage I.

Oxidation and reduction reactions ocurring simultaneously are called redox reactions. Oxidation involves loss of electrons while reduction involves gain of electrons. As a result, oxidation number of an atom increases during oxidation and decreases during reduction. The redox reaction may involve combination of atoms or molecules, displacement of metals or non-metals and disproportionation reactions. Redox reactions may be balanced by oxidation number method or ion-elecron method.

Answer the following questions :

D1. Which of the following represents oxidation ?

(*a*) $[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$

(*b*) $S + 2e^- \longrightarrow S^{2-}$

(*c*) $2Cl^- - 2e^- \longrightarrow Cl_2$

(*d*) $Sb^{5+} + 2e^- \longrightarrow Sb^{3+}$

D2. In the reaction :

$3Br_2 + 6CO_3^{2-} + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6HCO_3^-$

(*a*) Bromine is oxidised and carbonate is reduced

(*b*) Bromine is neither oxidised nor reduced

(*c*) Bromine is oxidised and water is reduced

(*d*) Bromine is both reduced and oxidised

D3. When copper is treated with concentrated nitric acid, nitric oxide and nitrogen dioxide are produced in equal volumes according to the following reaction :

$xCu + yHNO_3 \longrightarrow Cu(NO_3)_2 + NO + NO_2 + H_2O$

The coefficients x and y are

(*a*) 1 and 3 (*b*) 2 and 3

(*c*) 2 and 6 (*d*) 3 and 8

D4. A compound contains atoms of three elements A, B and C. If the oxidation number of A is +2, B is +5 and that of C is –2, then the possible formula of the compound is

(*a*) $A_3(BC_4)_2$ (*b*) $A_3(B_4C)_2$

(*c*) ABC_2 (*d*) $A_3(BC_3)_2$ *(CBSE P.M.T.2000)*

D5. In which of the following the change of oxidation states is not correctly represented ?

(*a*) $KMnO_4 + 5e^- \longrightarrow Mn^{2+}$

(*b*) $KMnO_4 + 2e^- \longrightarrow \frac{1}{2}Mn_2O_3$

(*c*) $KMnO_4 + 3e^- \longrightarrow MnO_2$

(*d*) $KMnO_4 + e^- \longrightarrow MnO_4^{2-}$

Answers

Passage I. **D1.** (*c*) **D2.** (*d*) **D3.** (*d*) **D4.** (*d*) **D5.** (*d*)

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Passage II.

Redox reactions play pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values.

Answer the following questions :

$I_2 + 2e^- \longrightarrow 2I^-$ $\quad E° = 0.54$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ $\quad E° = 1.36$

$Mn^{3+} + e^- \longrightarrow Mn^{2+}$ $\quad E° = 1.50$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\quad E° = 0.77$

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $\quad E° = 1.23$

Using these data, obtain the correct explanation for the following questions.

D6. Among the following, identify the correct statement.
- (*a*) Chloride ion is oxidised by O_2
- (*b*) Fe^{2+} is oxidised by iodide
- (*c*) Iodide ion is oxidised by chlorine
- (*d*) Mn^{2+} is oxidised by chlorine

D7. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because
- (*a*) O_2 oxidises Mn^{2+} to Mn^{3+}
- (*b*) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
- (*c*) Fe^{3+} oxidises H_2O to O_2
- (*d*) Mn^{3+} oxidises H_2O to O_2

D8. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in the presence of air gives a prussian blue precipitate. Hence, the blue colour is due to the formation of
- (*a*) $Fe_4[Fe(CN)_6]_3$ (*b*) $Fe_3[Fe(CN)_6]_2$
- (*c*) $Fe_4[Fe(CN)_6]_2$ (*d*) $Fe_3[Fe(CN)_6]_3$

(*I.I.T. 2007*)

Passage III.

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured iodometry.

Answer the following questions :

D9. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is
(*a*) Cl_2O (*b*) Cl_2O_7 (*c*) ClO_2 (*d*) Cl_2O_6

D10. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is
(*a*) 0.48 M (*b*) 0.96 M
(*c*) 0.24 M (*d*) 0.024 M (*I.I.T. 2012*)

Answers

Passage II. **D6.** (*c*) **D7.** (*d*) **D8.** (*a*) **Passage III.** **D9.** (*a*) **D10.** (*c*)

Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reasson is the corect explanation of the assertion.
(*b*) If both assertion and reason are CORRET, but reason is NOT THE CORRECT explanation of the assertion.
(*c*) If assertion is CORRECT, but reason is INCORRECT.
(*d*) If assertion is INCORRECT, but reason is CORRECT.
(*e*) If both assertion and reason are INCORRECT.

1. Assertion : Oxidation state of hydrogen in H_2O is +1 and in CaH_2 it is –1.
Reason : CaH_2 is metal hydride and for hybrides, hydrogen is assigned the oxidation state of –1.

2. Assertion : Oxidation number of C in HCHO is zero.
Reason : Formaldehyde is a covalent compound.

3. Assertion : Oxygen has oxidation state of –2 in both O_2 and O_3.
Reason : Oxygen is assigned an oxidation state of – 2 in almost all its compounds.

4. Assertion : Oxidation number of phosphorus in P_4 is zero.
Reason : Phosphorus has oxidation state zero in all its compounds.

5. Assertion : Redox reactions are also called neutralisation reactions.
Reason : The number of electrons gained or lost in the reaction are balanced.

6. Assertion : $3ClO^- \longrightarrow ClO_3^- + 2Cl^-$ is an example of dissociation reaction.
Reason : ClO^- gets oxidised as well as reduced.

Answers

1. (*a*) **2.** (*b*) **3.** (*d*) **4.** (*c*) **5.** (*d*) **6.** (*d*)

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7. **Assertion :** A substance which gets reduced can act as reducing agent.
   Reason : An oxidising agent itself gets oxidised.
8. **Assertion :** Copper sulphate solution is not stored in zinc vessel.
   Reason : Zinc forms complex with copper sulphate.
9. **Assertion :** The Daniell cell becomes dead after sometime.
   Reason : Oxidation potential of zinc anode decreases and that of copper cathode increases. *(AIIMS 2013)*
10. **Assertion :** In iodometric titrations, starch is used as an indicator.
    Reason : Starch is a polysaccharide.

Answers

7. (e) **8.** (c) **9.** (a) **10.** (b)

Integer Type Questions

Integer Type : The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. The difference in oxidation number of two types of sulphur atoms in $Na_2S_4O_6$ is *(I.I.T. 2011)*
2. How many moles of 'iodine' are liberated when 2 moles of $KMnO_4$ react with KI in acidic medium?
3. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is *(I.I.T. 2010)*
4. The oxidation number of S in H_2SO_5 is $+x$. The value of x is
5. The number of compounds among the following having O.N. of S as +6 is
   $S_2O_7^{2-}$, $Na_2S_2O_3$, H_2SO_3, HSO_4^-, $(NH_4)_2SO_4$, H_2SO_4, HSO_3^-, $S_4O_6^{2-}$
6. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with the evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is *(I.I.T. 2011)*

Answers

1. (5) **2.** (5) **3.** (3) **4.** (6) **5.** (4) **6.** (5)

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Which of the following is not an example of redox reaction ?
   (a) $CuO + H_2 \longrightarrow Cu + H_2O$
   (b) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
   (c) $2K + F_2 \longrightarrow 2KF$
   (d) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$
2. The more positive the value of E°, the greater is the tendency of the species to get reduced. Using the standard electrode potential of redox couples given below find out which of the following is the strongest oxidising agent.
   E° values : $Fe^{3+}|Fe^{2+} = +0.77$; $I_2(s)|I^- = +0.54$; $Cu^{2+}|Cu = +0.34$; $Ag^+|Ag = +0.80V$
   (a) Fe^{3+} (b) $I_2(s)$
   (c) Cu^{2+} (d) Ag^+
3. E° values of some redox couples are given below. On the basis of these values choose the correct option.
   E° values : $Br_2|Br^- = +1.09$; $Ag^+|Ag(s) = +0.80$; $Cu^{2+}|Cu(s) = +0.34$; $I_2(s)|I^- = +0.54$
   (a) Cu will reduce Br^- (b) Cu will reduce Ag
   (c) Cu will reduce I^- (d) Cu will reduce Br_2

Answers

1. (d) **2.** (d) **3.** (d)

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4. Using the standard electrode potential, find out the pair between which redox reaction is not feasible.

E° values : $Fe^{3+} | Fe^{2+} = +0.77$; $I_2 | I^- = +0.54$; $Cu^{2+} | Cu = +0.34$; $Ag^+ | Ag = +0.80$ V.

(*a*) Fe^{3+} and I^- (*b*) Ag^+ and Cu

(*c*) Fe^{3+} and Cu (*d*) Ag and Fe^{3+}

5. Thiosulphate reacts differently with iodine and bromine in the reactions given below :

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

$$S_2O_3^{2-} + 2Br_2 + 5H_2O \longrightarrow 2SO_4^{2-} + Br^- + 10H^+$$

Which of the following statements justifies the above dual behaviour of thiosulphate ?

(*a*) Bromine is a stronger oxidant than iodine.

(*b*) Bromine is a weaker oxidant than iodine.

(*c*) Thiosulphate undergoes oxidation by bromine and reduction by iodine in these reactions.

(*d*) Bromine undergoes oxidation and iodine undergoes reduction in these reactions.

6. The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following rules is not correct in this respect ?

(*a*) The oxidation number of hydrogen is always +1.

(*b*) The algebraic sum of all the oxidation numbers in a compound is zero.

(*c*) An element in the free or the uncombined state bears oxidation number zero.

(*d*) In all its compounds, the oxidation number of fluorine is –1.

7. In which of the following compounds, an element exhibits two different oxidation states ?

(*a*) NH_2OH (*b*) NH_4NO_3

(*c*) N_2H_4 (*d*) N_3H

8. Which of the following arrangements represent increasing oxidation number of the central atom ?

(*a*) CrO_2^-, ClO_3^-, CrO_4^{2-}, MnO_4^-

(*b*) ClO_3^-, CrO_4^{2-}, MnO_4^-, CrO_2^-

(*c*) CrO_2^-, ClO_3^-, MnO_4^-, CrO_4^{2-}

(*d*) CrO_4^{2-}, MnO_4^-, CrO_2^-, ClO_3^-

9. The largest oxidation number exhibited by an element depends on its outer electronic configuration. With which of the following outer electronic configurations the element will exhibit largest oxidation number ?

(*a*) $3d^14s^2$ (*b*) $3d^34s^2$ (*c*) $3d^54s^1$ (*d*) $3d^54s^2$

10. Identify disproportionation reaction

(*a*) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

(*b*) $CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$

(*c*) $2F_2 + 2OH^- \longrightarrow 2F^- + OF_2 + H_2O$

(*d*) $2NO_2 + 2OH^- \longrightarrow NO_2^- + NO_3^- + H_2O$

11. Which of the following elements does not show disproportionation tendency ?

(*a*) Cl (*b*) Br (*c*) F (*d*) I

Answers

4. (*d*) **5.** (*a*) **6.** (*a*) **7.** (*b*) **8.** (*a*) **9.** (*d*) **10.** (*d*) **11.** (*c*)

Multiple Choice Questions (Type-II)

12. Which of the following statement (*s*) is/are not true about the following decomposition reaction.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

(*a*) Potassium is undergoing oxidation

(*b*) Chlorine is undergoing oxidation

(*c*) Oxygen is reduced

(*d*) None of the species are undergoing oxidation or reduction

13. Identify the correct statement (*s*) in reflection to the following reaction :

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

(*a*) Zinc is acting as an oxidant

(*b*) Chlorine is acting as a reductant

(*c*) Hydrogen ion is acting as an oxidant

(*d*) Zinc is acting as a reductant

14. The exhibition of various oxidation states by an element is also related to the outer orbital electronic configuration of its atom. Atom(*s*) having which of the following outermost electronic configurations will exhibit more than one oxidation state in its compounds.

(*a*) $3s^1$ (*b*) $3d^14s^2$

(*c*) $3d^24s^2$ (*d*) $3s^23p^3$

15. Identify the correct statements with reference to the given reaction

$$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$$

(*a*) Phosphorus is undergoing reduction only.

(*b*) Phosphorus is undergoing oxidation only.

(*c*) Phosphorus is undergoing oxidation as well as reduction.

(*d*) Hydrogen is undergoing neither oxidation nor reduction.

16. Which of the following electrodes will act as anodes, when connected to Standard Hydrogen Electrode ?

(*a*) Al/Al^{3+} $E° = -1.66$ V

(*b*) Fe/Fe^{2+} $E° = -0.44$ V

(*c*) Cu/Cu^{2+} $E° = +0.34$ V

(*d*) $F_2(g)/2F^-(aq)$ $E° = +2.87$ V

Answers

12. (*a, b, c, d*) **13.** (*c, d*) **14.** (*b, c, d*) **15.** (*c, d*) **16.** (*a, b*)

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Matching Type Questions

Q. 17. Match Column I with Column II for the oxidation states of the central atoms.

Column I	*Column II*
(*i*) $Cr_2O_7^{2-}$	(*a*) + 3
(*ii*) MnO_4^-	(*b*) +4
(*iii*) VO_3^-	(*c*) +5
(*iv*) FeF_6^{3-}	(*d*) +6
	(*e*) +7

Q. 18. Match the items in Column I with relevant items in Column II.

Column I	*Column II*
(*i*) Ions having positive charge	(*a*) +7
(*ii*) The sum of oxidation number of all atoms in a neutral molecule	(*b*) –1
(*iii*) Oxidation number of hydrogen ion (H^+)	(*c*) +1
(*iv*) Oxidation number of fluorine in NaF	(*d*) 0
(*v*) Ions having negative charge	(*e*) Cation
	(*f*) Anion

Answers

17. (*i*) – (*d*); (*ii*) – (*e*); (*iii*) – (*c*); (*iv*) – (*a*) **18.** (*i*) – (*e*); (*ii*) – (*d*); (*iii*) – (*c*); (*iv*) – (*b*), (*v*) – (*f*)

Assertion and Reason Type Questions

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct option out of the choices given below each question.

(*a*) Both A and R are true and R is the correct explanation of A.

(*b*) Both A and R are true but R is not the correct explanation of A.

(*c*) A is true but R is false.

(*d*) Both A and R are false.

19. Assertion (A) : Among halogens fluorine is the best oxidant.

Reason (R) : Fluorine is the most electronegative atom.

20. Assertion (A) : In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

Reason (R) : Oxidation state of manganese changes from +2 to +7 during the reaction.

21. Assertion (A) : The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

Reason (R) : The oxygen of peroxide is in –1 oxidation state and it is converted to zero oxidation state in O_2 and –2 oxidation state in H_2O.

22. Assertion (A) : Redox couple is the combination of oxidised and reduced form of a substance involved in an oxidation or reduction half cell.

Reason (R) : In the representation $E^o_{Fe^{3+}/Fe^{2+}}$ and $E^o_{Cu^{2+}/Cu}$, Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu are redox couples.

Answers

19. (*b*) **20.** (*c*) **21.** (*a*) **22.** (*b*)

Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A2. (*c*) : $x - 2 \times 4 = -3$ $\therefore x = +5$

A3. (*d*) : $x - 8 = -1$ $\therefore x = +7$

A4. (*a*) : CH_3OH : $x + 3 - 2 + 1$ $\therefore x = -2$

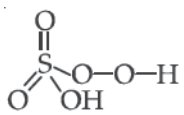
CH_2O : $x + 2 - 2$ $\therefore x = 0$

HCOOH : $+1 + x - 4 + 1$ $\therefore x = +2$

C_2H_2 : $2x + 2$ $\therefore x = -1$

A5. (*c*) : Na_2S_2 $+ 2 + 2x = 0$ $\therefore x = -1$

A6. (*b*) : H_2SO_5 has one peroxide bond as



So, it may be written as

$H_2S(O_2)O_3$

$+2 + x - 2 + 3(-2) = 0$ $\therefore x = +6$

A7. (*a*) : Sodium exists in elemental form.

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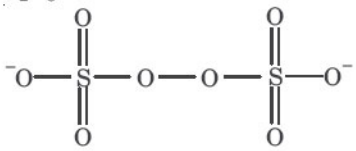
A8. (*d*) : $Cl_2 + 2\,OH^- \longrightarrow OCl^- + Cl^- + H_2O$
O.N. of Cl changes from 0 to +1 (in OCl^-) and –1 in (Cl^-).

A9. (*c*) : $S_2O_8^{2-}$ has structure



2 O atoms have peroxide linkage so it may be written as $S_2(O_2)\,O_6^{2-}$
$\therefore\ 2x - 2 + 6(-2) = -2 \qquad \therefore\ x = +6$

A10. (*c*) : In CH_3CHO, $2x + 4 - 2 = 0 \qquad \therefore\ x = -1$

A11. (*d*) : V(+2), Br + 3 in $(BrO_2)^-$ so it exists as $V^{II}(Br^{III}O_2)_2$

A12. (*c*) : $HN_3 \qquad 1 + 3x = 0 \qquad \therefore\ x = -1/3$

A13. (*d*) : *a* (+2.5), *b* (+1), *c* (0), *d* (+7)

A15. (*a*) : $CuO + \overset{+3}{2NH_3} \longrightarrow \overset{0}{N_2} + 3H_2O + Cu$

$-6e^-$

Loss of $6e^-$ for 1 mol of N_2

A16. (*d*) : In oxidation, there is increase in O.N.

A17. (*c*) : O.N. of P changes from zero to –3 in PH_3 and +1 in NaH_2PO_2. Therefore, it undergoes disproportionation.

A20. (*a*) : $+2 + 2x = 0 \ \therefore\ x = -1$

A21. (*c*) : $Ba(H_2PO_2)_2$

$+2 + 2(+2 + x - 4) = 0$

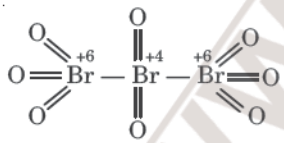
$+2 + 4 + 2x - 8 = 0 \qquad \therefore\ x = +1$

A23. (*d*) : The O.N. of bromine decreases from 0 to –1 (in Br^-) and increases from 0 to +5 (in BrO_3^-).

A25. (*d*) : The calculated O.N. of Br in Br_3O_8 is

$3x + 8(-2) = 0$ or $x = \dfrac{16}{3}$

Actual O.N. of different Br atoms is



A26. (*b*) : The O.N. of Br increases from 0 to +1 in (HOBr) and decreases from 0 to –1 (in HBr). Therefore it is oxidised as well as reduced.

A28. (*a*) : O.N. are SO_3^{2-}(+4), $S_2O_4^{2-}$(+3), $S_2O_6^{-2}$(+5)
$\therefore$ Correct order
$S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

A31. (*a*) : The balanced equation is

$4\,Zn + NO_3^- + 7H_2O \longrightarrow 4Zn^{2+} + NH_4^+ + 10\,OH^-$

A35. (*a*) : The balanced equation is

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

A37. (*a*) : Since the reduction potential of Y is greater than that of X but lower than that of Z. Therefore, Y will oxidize X but not Z.

B. *mcq from competitive examinations*

B3. (*a*) : $IO_3^- + 5I^- + 6H^+ \longrightarrow 3H_2O + 3I_2$

B4. (*a*) : $5FeC_2O_4 + 3MnO_4^- + 24\,H^+ \longrightarrow 5Fe^{3+} + 10CO_2 + 3Mn^{2+} + 12H_2O$

5 mol of $FeC_2O_4 \equiv 3$ mol of MnO_4^-

$\therefore$ 1 mol of $FeC_2O_4 \equiv \dfrac{3}{5}$ mol of MnO_4^-

$\equiv 0.6$ mol of MnO_4^-

B5. (*c*) : Higher the reduction potential, larger is its tendency to get reduced and hence stronger is the reducing agent.

B7. (*d*) : $\overset{+8}{H_2S}O_5 > \overset{+4}{H_2S}O_3 > \overset{+2}{S}Cl_2 > \overset{-2}{H_2S}$

B9. (*c*) : As the electrode potential decreases, reducing power decreases.

$Z > X > Y$

B10. (*c*) : $N_2H_4 \Rightarrow 2x + 4\,(+1)$ or $2x + 4 = 0 \ \therefore\ x = -2$

$NH_3 \Rightarrow x + 3\,(+1) = 0$ or $x + 3 = 0 \ \therefore\ x = -3$

$N_3H \Rightarrow 3x + 1\,(+1) = 0$ or $3x + 1 = 0 \ \therefore\ x = -1/3$

$NH_2OH \Rightarrow x + 2 + (-2) + 1 = 0$ or $x + 1 = 0$

$\therefore \qquad x = -1$

Thus, highest oxidation state is –1/3.

B11. (*c*) :

$$\overset{+1+5-2}{KClO_3} + \overset{COOH}{\underset{COOH}{|}} + \overset{+6}{H_2SO_4} \longrightarrow \overset{+6}{K_2SO_4} + \overset{-1}{KCl} + CO_2 + H_2O$$

Maximum change in oxidation number of chlorine *i.e.*, from + 5 to – 1.

B13. (*b*) : $\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow \overset{-3}{PH_3} + 3NaH_2\overset{+1}{P}O_2$

In this reaction, P is oxidised to NaH_2PO_2 and reduced to PH_3. This is disproportionation reaction.

B14. (*a*) : Oxidation of iron in $Fe(CO)_5$ is zero.
There is no change in oxidation number of Fe in

$Fe + 5CO \longrightarrow Fe(CO)_5$

Hence, it does not involve oxidation of iron.

B16. (*b*) : The correct balanced equation is

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

B17. (*c*) :

$\overset{+7}{KMnO_4} + e^- \longrightarrow \overset{+6}{MnO_4^{2-}}\,(1e)$

$\overset{+7}{KMnO_4} + 3e^- \longrightarrow \overset{+4}{MnO_2}\,(3e)$

$\overset{+7}{KMnO_4} + 4e^- \longrightarrow \overset{+3}{\tfrac{1}{2}Mn_2O_3}\,(4e)$

$\overset{+7}{KMnO_4} + 5e^- \longrightarrow \overset{+2}{Mn^{2+}}\,(5e)$

B18. (*d*) : The balanced equation is :

$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$

B19. (*a*) : $E^\circ_{cell} = E^\circ\,(Fe^{3+}\,|\,Fe^{2+}) - E^\circ\,(Sn^{2+}\,|\,Sn)$
$= 0.77 - (-0.14) = +0.91$ V

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B20. (*a*) : For the reaction :

$$Zn\,(s) + 2H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)$$

$$E = E^\circ - \frac{RT}{nF} ln \frac{[Zn^{2+}](p_{H_2})}{[H^+]^2}$$

On adding H_2SO_4, the $[H^+]$ increases. This will increase the value of E and, therefore, reaction proceeds more to the right.

B21. (*d*) : $K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$

$2KCl + H_2SO_4 \longrightarrow 2KHSO_4 + 2HCl\ ] \times 2$

$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O\ ] \times 2$

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$$

B22. (*c*) : HClO disproportionates as :

$$\overset{+1}{3HOCl} \longrightarrow \overset{-1}{2HCl} + \overset{+5}{HClO_3}$$

B23. (*d*) : $H-\overset{\overset{O}{\|}}{C}-H$ or HCHO

$+1 + x - 2 + 1 = 0$

or $x = 0$

B24. (*b*) :For (*a*) $E^\circ = -0.34 + 0.80 = 0.46$ V

(*b*) $E^\circ = 0.76 + 0.80 = 1.56$ V

(*c*) $E^\circ = -0.25$ V

(*d*) $E^\circ = 0.76 + 0.34 = 1.00$ V

(*e*) $E^\circ = 0.76$ V

$\therefore$ Correct answer (*b*).

B26. (*a*) : $K_2Cr_2O_7 + H_2SO_4 + \overset{+4}{3S}O_2 \rightarrow \overset{+6}{K_2SO_4} + Cr_2(SO_4)_3 + H_2O$

Oxidation number of S changes from +4 to +6.

B28. (*c*) : $2KOH + \overset{0}{Cl_2} \longrightarrow \overset{-1}{KCl} + \overset{+1}{KOCl} + H_2O$

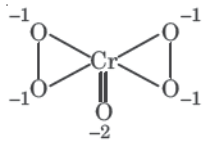
Oxidation (0 → +1); Reduction (0 → −1)

B31. (*a*) : $\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow 3NaH_2\overset{+1}{P}O_2 + \overset{-3}{P}H_3$

Oxidation (0 → +1); Reduction (0 → −3)

In this, the same substance undergoes oxidation as well as reduction and therefore, it is an example of disproportionation reaction.

B32. (*b*) :



$x - 6 = 0$

$\therefore\ x = +6$

B33. (*b*) : Here NO is in +1 oxidation state so that

$x + 5\,(0) + 1 = +2$

$\therefore\ x = +1$

B34. (*d*) : $KMnO_4$ can oxidise HCl also into Cl_2 and itself gets reduced to Mn^{2+}.

B40. (*d*) : Chromite ore is $FeCr_2O_4$.

B42. (*b*) : $\overset{+2}{2S_2O_3}^{2-} + \overset{0}{I_2} \longrightarrow \overset{+2.5}{S_4O_6} + \overset{-1}{2I^-}$

Change in O.N. per mol = 1 × 2 = 2

Change in O.N. per mol = 0.5 × 2 = 1

Equivalent wt. of $Na_2S_2O_3 = \frac{M_1}{1}$

Equivalent wt. of $I_2 = \frac{M_2}{2}$

B43. (*d*) : $\overset{-2}{H_2S} + \overset{-1}{H_2O_2} \longrightarrow \overset{0}{S} + \overset{-2}{2H_2O}$

Reduction (Oxidising agent); Oxidation (reducing agent)

B44. (*c*) : Metals get deposited after undergoing reduction on cathode. Higher the value of reduction potential, more is the tendency to get reduced. Order of E° values : Ag > Hg > Cu.

Hence, sequence of deposition : Ag, Hg, Cu.

B45. (*c*) : H_2O_2 gets reduced to H_2O and acts as an oxidising agent.

B46. (*a*) : $E^\circ_{cell} = E^\circ_{A^{2+}|A} - E^\circ_{X^{2+}|X}$

$= 0.34 - (-2.37) = 2.71$ V

B47. (*d*) : MnO_4^- is the strongest oxidising agent because it has highest reduction potential value.

B48. (*c*) : $[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

B49. (*c*) : O.N. of Br has increased from –1 to 0 and it is oxidised. Hence, it acts as a reducing agent.

B50. (*b*) : $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow Cr^{3+} + 7H_2O$

Oxidation state of Cr in $Cr_2O_7^{2-} = +6$

Oxidation state of Cr in $Cr^{3+} = +3$

Change in oxidation state = 3

B51. (*c*) : Oxidation state of N in hydrazine:

N_2H_4

$2x + 4 = 0$ or $x = -2$

1 mol of N_2H_4 loses 10 mol of electrons. Therefore, one nitrogen loses 5 electrons. Thus, the oxidation state of N in new compound is = –2 + 5 = + 3

B52. (*c*) : $\overset{+1}{3ClO^-} \longrightarrow \overset{+5}{ClO_3^-} + \overset{-1}{2Cl^-}$

Reduction (+1 → −1); Oxidation (+1 → +5)

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The oxidation state of Cl decreases from +1 to –1 (reduction) and increases from +1 to +5 (oxidation). It is a disproportionation reaction.

B53. (*c*) : $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

B54. (*b*) : The balanced reaction is :

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Therefore, $x = 2, y = 5, m = 2, n = 10$

B55. (*c*) : Conc. HNO_3 oxidises I_2 to iodic acid (HIO_3)
Oxidation state of iodine in HIO_3 is +5

B56. (*b*) : $M^+ + e^- \longrightarrow M \quad E^\circ = +0.44\ V \quad .....(i)$
$X + e^- \longrightarrow X^- \quad E^\circ = +0.33\ V \quad .....(ii)$
Subtracting eqn. (*ii*) from eqn. (*i*)
$M^+ + X^- \longrightarrow M + X \quad E^\circ = +0.11\ V$
Since E° is positive, the reaction is spontaneous.

B57. (*a*) : MnO_4^- will oxidise Cl^- ion according to the reaction.

$$2KMnO_4 + 16H^+ + 16\ Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5\ Cl_2$$

The corresponding cell is
$Pt \mid Cl_2\ (g) \mid Cl^-\ (aq) \parallel MnO_4^-(aq), Mn^{2+}, H^+ \mid Pt$
$E^\circ_{cell} = E^\circ\ (cathode) - E^\circ\ (anode)$
$= 1.51 - 1.40 = 0.11\ V$
Since E°_{cell} is +ve, the above reaction is feasible. Therefore, MnO_4^- will oxidise both Fe^{2+} and Cl^- ions in aqueous medium. Thus, quantitative estimation of $Fe(NO_3)_2$ is not suitable.

B58. (*b*) : MnO_4^-(+7) and CrO_2Cl_2(+6) have highest oxidation states.

B59. (*b*) : Oxidation state of nitrogen in compounds is HNO_3 (+5), NO(+2), N_2(0), NH_4Cl (–3).

C. *mcq with more than one correct answer*

C9. (*a, b, d*). The balanced chemical equation is:

$$6\overset{-1}{I^-} + ClO_3^- + 6H_2\overset{+6}{S}O_4 \longrightarrow Cl^- + 6H\overset{+6}{S}O_4^- + 3\overset{0}{I_2} + 3H_2O$$

O.N. increases (oxidised)

(*a*) Stoichiometric coefficient of HSO_4^- is 6.
(*b*) O.N. of I^- increases from –1 to 0 and hence it is oxidised.
(*d*) H_2O is one of the products.

D. *mcq based on comprehension*

D6. (*c*) : On calculating the e.m.f. of the cells, we find that only the e.m.f. of the cell involving oxidation of I^- ion by Cl_2 is +ve and option (*c*) is correct.

$2I^- \longrightarrow I_2 + 2e^- \quad E^\circ = -0.54V$
$Cl_2 + 2e^- \longrightarrow 2Cl^- \quad E^\circ = +1.36V$
$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2 \quad E^\circ = 1.36 - 0.54 = 0.82\ V$

D7. (*d*) : Only the e.m.f. of the cell involving the oxidation of H_2O to O_2 by Mn^{3+} is +ve.

$Mn^{3+} + e^- \longrightarrow Mn^{2+}] \times 4 \quad E^\circ = +1.50V$
$2H_2O \longrightarrow 4H^+ + O_2 + 4e^- \quad E^\circ = -1.23V$
$4Mn^{3+} + 2H_2O \longrightarrow 4Mn^{2+} + O_2 + 4H^+ \quad E^\circ = +0.27\ V$

D8. (*a*) : $Na + C + N \longrightarrow NaCN$
Sodium fusion extract
$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$
In the presence of air, Fe^{2+} ions get oxidised to Fe^{3+} ions.

$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad E^\circ = -0.77\ V$
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \quad E^\circ = -1.23\ V$
$4Fe^{2+} + 4H^+ + O_2 \longrightarrow 4Fe^{3+} + 2H_2O \quad E^\circ_{Cell} = +0.46\ V$

Fe^{3+} ions then combine with $[Fe(CN)_6]^{4-}$ ion to form ferric ferrrocynide which has prussian blue colour.

$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$ (Prussian blue)

D9. (*a*) : The active constituent of bleaching powder or bleaching solution is $Ca(OCl)_2$. The anion of this salt is OCl^- and therefore, the corresponding acid is HOCl. The anhydride of this acid is Cl_2O as

$$2HOCl \longrightarrow H_2O + Cl_2O$$

D10. (*c*) : Applying normality equation,

$N_1V_1 \equiv N_2V_2$
$Ca(OCl)_2 = Na_2S_2O_3$
$N_1 \times 25 = 0.25 \times 48$
$N_1 = \frac{0.25 \times 48}{25} = 0.48\ N$

The reaction is

$Ca(OCl)_2 + 4H^+ + 2e^- \longrightarrow Ca^{2+} + 2H_2O + Cl_2 \quad ...(i)$
$2KI + Cl_2 \longrightarrow 2KCl + I_2$
$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$
$Ca(OCl)_2 + 4H^+ + 2e^- + 2KI + 2Na_2S_2O_3 \longrightarrow Ca^{2+} + 2H_2O + 2KCl + Na_2S_4O_6 + 2NaI \quad ...(ii)$

Since the eqn. (*i*) involves change of $2e^-$,

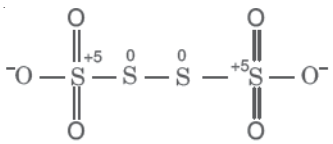
$$\text{Eq. wt. of } Ca(OCl)_2 = \frac{\text{Mol. wt}}{2}$$

$$\therefore \quad \text{Molarity} = \frac{\text{Normality}}{2} = \frac{0.48}{2} = 0.24$$

$\therefore$ Molarity of household bleach = 0.24 M

Integer Type Answers

1. (5) : O.N. of different S atoms in $Na_2S_4O_6$ is



Difference in O.N. = 5 – 0 = 5

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Competition File

2. (5) : $2MnO_4^- + 10\ I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

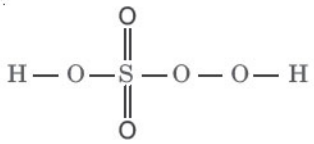
Thus, 2 mol of $KMnO_4$ react with KI to liberate 5 moles of I_2.

3. (3) : $Be_n\ Al_2\ Si_6\ O_{18}$

$n(+2) + 2(+3) + 6(+4) + 18(-2) = 0$

$2n + 6 + 24 - 36 = 0$ or $2n = 6$ $\therefore$ $n = 3$

4. (6) :



In peroxide bond, the oxidation state of O is – 1

$H_2S(O_2)O_3$

$2(+1) + x + 2(-1) + 3(-2) = 0$ $\therefore$ $x = +6$

5. (4) : O.N. of S is + 6 in $S_2O_7^{2-}$, HSO_4^-, $(NH_4)_2SO_4$, H_2SO_4

6. (5) : $3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$

NCERT Exemplar Problems : MCQs Type-I

2. (*d*) : $Ag^+|Ag$ is most positive and therefore, Ag^+ is the strongest oxidising agent.

3. (*d*) : Copper will reduce Br_2 because $E°(1.09 - 0.34 = 0.75V)$ is +ve.

$$2Cu + 2Br_2 \longrightarrow 2Cu\ Br_2$$

4. (*d*) : The reaction : $Ag + Fe^{3+} \longrightarrow Ag^+ + Fe^{2+}$ is not feasible because $E°\ (0.77 - 0.80 = -0.03)$ is negative.

6. (*a*) : O.N. of hydrogen is not always +1. The O.N. of hydrogen in hydrides is –1 and in H_2, it is zero.

7. (*b*) : NH_4NO_3 exists as NH_4^+ and NO_3^- ions. The O.N. of N in NH_4^+ is – 3 and NO_3^-, O.N. is +5.

8. (*a*) : $\overset{+3}{CrO_2^-}$, $\overset{+5}{ClO_3^-}$, $\overset{+6}{CrO_4^{2-}}$ and $\overset{+7}{MnO_4^-}$

9. (*d*) : The element having electronic configuration $3d^54s^2$ can exhibit maximum O.N. of +7.

10. (*d*) : $2NO_2 + 2OH^- \longrightarrow NO_2^- + NO_3^- + H_2O$ is a disproportionation reaction because N is both oxidised as well as reduced. O.N. of N increases from +4 (in NO_2) to +3 (in NO_2^-).

11. (*c*) : Fluorine being most electronegative exhibits only –1 oxidation state.

NCERT Exemplar Problems : MCQs Type-II

12. (*a, b, c, d*) : $\overset{+1\,+5\,-2}{2KClO_3} \longrightarrow \overset{+1\,-1}{2KCl} + \overset{0}{3O_2}$

(*a*) Since O.N. of potassium does not change, it neither undergoes oxidation nor reduction.

(*b*) O.N. of Cl decreases from +5 ($KClO_3$) to –1 (in KCl), therefore, it is undergoing reduction.

(*c*) O.N. of O increases from –2 (in $KClO_3$) to zero (in O_2), therefore, O is oxidised.

(*d*) This statement is not correct because Cl is undergoing reduction and O is undergoing oxidation.

13. (*c, d*) : $\overset{0}{Zn} + 2\overset{+1\ -1}{HCl} \longrightarrow \overset{+2\ -1}{ZnCl_2} + \overset{0}{H_2}$

(*a*) The O.N. of Zn increases from 0 to +2 (in $ZnCl_2$) and therefore, Zn acts as a reductant and not as an oxidant. Hence, option is not correct.

(*b*) The O.N. of Cl does not change and therefore, it neither acts as a reductant nor an oxidant. Hence, option is not correct.

(*c*) The O.N. of H decreases from +1 in H^+ to 0 in H_2. Therefore H^+ acts an oxidant. This option is correct.

(*d*) Zinc acts as reductant because its O.N. changes from 0 to +2. This option is correct.

14. (*b, c, d*) : The elements having *b*, *c* and *d* configuration can exhibit variable oxidation states.

15. (*c, d*) : $\overset{0}{P_4} + 3\overset{-2\,+1}{OH^-} + 3\overset{+1\ -2}{H_2O} \longrightarrow \overset{-3\,+1}{PH_3} + 3H_2PO_2^-$

Because O.N. of P increases from $0(P_4)$ to +1 ($H_2PO_2^-$) and decreases from $0(P_4)$ to –3 (PH_3), therefore, P has undergone both oxidation as well as reduction. Option (*c*) is correct. Option (*d*) is also correct because O.N. of H remains +1 in all the compounds and hence hydrogen is undergoing neither oxidation nor reduction.

16. (*a, b*) : The electrodes having negative electrode potentials are stronger reducing agents than H_2 gas and therefore, will act as anodes.

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Unit Practice Test

for Board Examination

Time Allowed: 1 Hr. ***Maximum Marks: 25***

1. Calculate the oxidation number of sulphur in $S_2O_8^{2-}$. (1)

2. Identify the oxidising and reducing agent in the following :

$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$ (1)

3. Give one example each in which the oxidation state of oxygen is –1 and +2. (1)

4. Define a disproportionation reaction. (1)

5. Can the reaction:

$Cr_2O_7^{2-} + H_2O \longrightarrow 2CrO_4^{2-} + 2H^+$

be regarded as a redox reaction or not ? (1)

6. Out of Al and Ag vessel, which one will be more suitable to store 1M HCl solution and why?

$E°(Al^{3+} \mid Al) = -1.66$ V, $E°(Ag^+ \mid Ag) = +0.80$ V (2)

7. So that the following reactions are redox reactions :

(*i*) $Fe_2O_3 + 3\,CO \longrightarrow 2Fe(s) + 3CO_2$

(*ii*) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

8. The compound AgF_2 is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why? (2)

9. Consider the reactions :

$2S_2O_3^{2-}(aq) + I_2(s) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

$S_2O_3^{2-}(aq) + 2Br_2(l) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$

Why does the same reductant, thiosulphate react differently with iodine and bromine. (2)

10. Depict the galvanic cell in which the reaction:

$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

takes place. Further show

(*i*) which electrode is negatively charged

(*ii*) individual reaction at each electrode. (3)

11. Permanganate (VII) ion, MnO_4^- in basic solution oxidises iodide ion, I^- to produce molecular iodine (I_2) and manganese (IV) oxide (MnO_2). Write a balanced ionic equation to represent this redox reaction. (3)

12. Balance the following equations by oxidation number method

(*i*) $Fe^{2+} + Cr_2O_7^{2-} + H^+ \longrightarrow Fe^{3+} + Cr^{3+} + H_2O$

(*ii*) $C_6H_6 + O_2 \longrightarrow CO_2 + H_2O$ (3)

13. (*a*) Fluorine reacts with ice and results in the following reaction :

$H_2O(s) + F_2(g) \longrightarrow HF(g) + HO(g)$

Justify that this reaction is a redox reaction.

(*b*) Calculate the oxidation number of sulphur in H_2SO_5.

Suggest structure and account for the fallacy. (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part II of the book.

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UNIT 9

HYDROGEN

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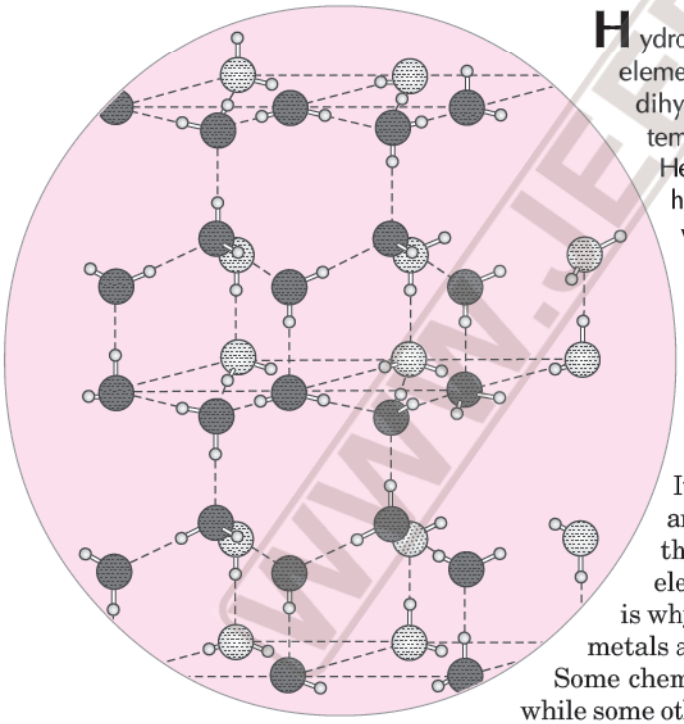

Hydrogen is the first element in the periodic table and is the lightest element known. It exists as a diatomic molecule H_2 and is called dihydrogen. The atomic form of hydrogen exists only at high temperatures. It was discovered by *Henry Cavendish* in 1766. He prepared the gas by treating iron with dil. H_2SO_4. Its name hydrogen was proposed by *Lavoisier* because it produces water on burning with oxygen (In Greek : *hydro* means water, *gene* means producing). Hydrogen forms a very large number of compounds and is of great industrial importance.

UNIQUE POSITION OF HYDROGEN IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table. Its atomic number is 1. It has one proton and one electron and it has the electronic configuration $1s^1$. Its position in the periodic table is shown in Fig. 1. In the normal elemental form, it exists as a diatomic molecule (H_2). That is why, it is also called **dihydrogen**. It resembles both alkali metals and halogens and, therefore, its position is ***anomalous***. Some chemists have argued for its placement with alkali metals while some other chemists have proposed its inclusion with halogens.

Resemblances with Alkali Metals

Hydrogen resembles alkali metals such as lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs) and francium (Fr) of group I of the periodic table in the following respects :

1. Electronic configuration. Hydrogen like alkali metals has one electron in its valence shell. For example,

H (Z = 1) : $1s^1$
Li (Z = 3) : [He] $2s^1$
Na (Z = 11) : [Ne] $3s^1$
K (Z = 19) : [Ar] $4s^1$, etc.

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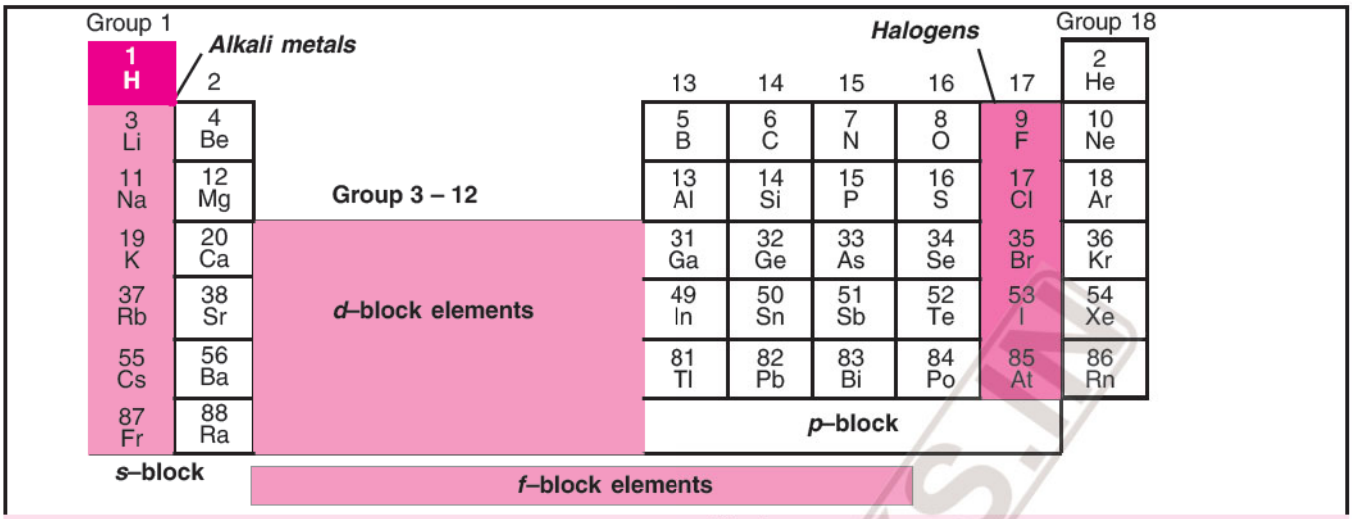

Fig. 1. Position of hydrogen

2. Electropositive character. Hydrogen like alkali metals is electropositive because it can lose one electron readily to form hydrogen ion (H^+) as

$$H \longrightarrow H^+ + e^-$$
$$1s^1 \qquad 1s^0 \text{ (proton)}$$
$$Na \longrightarrow Na^+ + e^-$$
$$[Ne]\ 3s^1 \qquad [Ne]$$

3. Valency and oxidation state. Like alkali metals, hydrogen also shows an oxidation state of +1 in its compounds. For example,

H^+Cl^-	$Na^+ Cl^-$	K^+Cl^-
Hydrogen chloride	Sodium chloride	Potassium chloride

4. Combination with electronegative elements. Like alkali metals, hydrogen forms binary compounds with electronegative elements such as halogen, oxygen and sulphur. For example,

Halides	: HCl	NaCl, KCl, etc.
Sulphides	: H_2S	Na_2S, K_2S, etc.
Oxides	: H_2O	Na_2O, K_2O, etc.

With oxygen, hydrogen also forms hydrogen peroxide (H_2O_2). Alkali metals also form peroxides e.g. Na_2O_2 (sodium peroxide), etc.

5. Liberation at cathode. When the fused salts of alkali metals are electrolysed, metal ions are liberated at the cathode. In a similar manner, hydrogen is liberated at the cathode on subjecting the aqueous solutions of its salts to electrolysis :

$$2HCl\ (aq) \xrightarrow{\text{Electrolysis}} \underset{\text{(At cathode)}}{H_2} + Cl_2$$

$$2NaCl\ (molten) \xrightarrow{\text{Electrolysis}} \underset{\text{(At cathode)}}{2Na} + Cl_2$$

6. Strong reducing agent. Like alkali metals, hydrogen acts as a *strong reducing agent*.

$$Fe_3O_4 + 4H_2 \xrightarrow{\text{Heat}} 3Fe + 4H_2O$$
$$B_2O_3 + 6K \xrightarrow{\text{Heat}} 2B + 3K_2O$$

Resemblances with Halogens

Hydrogen also resembles with halogens *i.e.*, fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) of group 17 of the periodic table. Some of its characteristics which show resemblance with halogens are given below :

1. Electronic configuration. Like halogens, hydrogen has only one electron less than the nearest noble gas configuration.

H : $1s^1$	He : $1s^2$
F : $1s^2\ 2s^2\ 2p^5$	Ne : $1s^2\ 2s^2\ 2p^6$
Cl : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	Ar : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

2. Ionisation enthalpy. The ionisation enthalpy of hydrogen is quite close to that of halogens, *e.g.*,

H : 1312 kJ mol^{-1}	F : 1680 kJ mol^{-1}
	Cl : 1255 kJ mol^{-1}
	Br : 1143 kJ mol^{-1}

The ionisation enthalpy of hydrogen and halogens are much higher than those of alkali metals:

Li : 520 kJ mol^{-1}
Na : 496 kJ mol^{-1}
K : 419 kJ mol^{-1}

3. Electronegative character. Hydrogen like halogens has tendency to accept electron to form monovalent anion. By accepting an electron hydrogen as well as halogens acquire noble gas configurations :

$$\underset{1s^1}{H} + e^- \longrightarrow \underset{1s^2}{H^-}\text{ (He gas configuration)}$$
$$\underset{[He]\ 2s^22p^5}{F} + e^- \longrightarrow \underset{[He]\ 2s^22p^6}{F^-}\text{ (Ne gas configuration)}$$
$$\underset{[Ne]\ 3s^23p^5}{Cl} + e^- \longrightarrow \underset{[Ne]\ 3s^23p^6}{Cl^-}\text{ (Ar gas configuration)}$$

4. Oxidation state. Like halogens, hydrogen exhibits oxidation state of –1 in its compounds.

$Na^+ H^-$	$Na^+ Cl^-$
Sodium hydride	Sodium chloride

5. Diatomic nature. Hydrogen molecule (H_2) is diatomic like halogen molecules (F_2, Cl_2, Br_2, I_2).

6. Liberation at anode. When fused alkali metal hydrides such as lithium or sodium hydride is electrolysed, hydrogen is liberated at the anode. This is in the same way as halogens are liberated at anode

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when fused alkali metal halides are electrolysed.

$$2NaH\ (molten) \xrightarrow{\text{Electrolysis}} 2Na\ (l) + \underset{\text{At anode}}{H_2\ (g)}$$

$$2NaCl\ (molten) \xrightarrow{\text{Electrolysis}} 2Na\ (l) + \underset{\text{At anode}}{Cl_2\ (g)}$$

7. Non-metallic nature. Like halogens, hydrogen is non–metallic in nature.

8. Nature of compounds. Like halogens, hydrogen combines with non-metals such as carbon, silicon, germanium, etc. to form **covalent compounds**. For example,

CH_4, SiH_4, GeH_4	Compounds of hydrogen
CCl_4, $SiCl_4$, $GeCl_4$	Compounds of halogens

Though hydrogen resembles alkali metals and halogens in many respects yet it is different from these in some respects. Hydrogen has none of the metallic characteristics* like alkali metals and its resemblance to halogens is only slight. The proton, H^+ has very small size about 1.5×10^{-3} pm compared to normal atomic and ionic sizes of 50 to 220 pm respectively. As a result, H^+ does not exist freely and is always associated with other atoms or molecules.

Some of its differences from alkali metals and halogens are discussed below.

Differences from Alkali Metals

Hydrogen differs in some of its characteristics from alkali metals. Some of these differences are :

1. Ionisation enthalpy. Ionisation enthalpy of hydrogen is very high in comparison to alkali metals. For example,

IE of H = 1312 kJ mol^{-1}

IE of Li = 520 kJ mol^{-1}, IE of Na = 495 kJ mol^{-1}, IE of K = 418 kJ mol^{-1}

2. Non-metallic character. Alkali metals are typical metals while hydrogen is non-metal.

3. Atomicity. Hydrogen is diatomic (H_2) whereas alkali metals are monoatomic.

4. Nature of compounds. The compounds of hydrogen are predominantly *covalent* while those of alkali metals are ionic. For example, HCl is covalent while NaCl is ionic.

The oxides of alkali metals are **basic** while hydrogen oxide (H_2O) is **neutral**.

Li_2O, Na_2O, K_2O, etc. : basic ; H_2O : neutral.

Differences from Halogens

Though hydrogen resembles halogens in many respects, yet it differs also in certain respects. Some of the important differences between hydrogen and halogens are given below :

1. Less tendency for hydride formation. Hydrogen has less tendency to take up electron to form hydride ion (H^-) as compared to the halogens which form halide ions (X^-) very easily.

2. Absence of unshared pairs of electrons. The hydrogen and the halogens are diatomic in nature in which the atoms are held by covalent bonds. However, hydrogen atoms do not possess any unshared electron pairs whereas there are three unshared electron pairs on each halogen atom in its molecule.

H — H	:Cl — Cl:
Hydrogen molecule	Chlorine molecule

3. Nature of oxides. The oxides of halogens are acidic while hydrogen oxide (H_2O) is neutral.

Cl_2O_7	H_2O
Acidic	Neutral

From the above discussion, it is clear that hydrogen is unique in its behaviour because it resembles alkali metals as well as halogens. Therefore, it is difficult to assign any definite position to it in the periodic table. Thus, the position of hydrogen in the periodic table is anomalous and *it is best placed separately in the periodic table of elements*.

OCCURRENCE OF HYDROGEN

Hydrogen is the most abundant element in the universe (about 70% of the total mass of the universe) and is also common on earth. In the free state, hydrogen is present in some volcanic gases and in the outer atmosphere of the sun and other stars of the universe. About half the mass of sun and some other stars is due to hydrogen. Jupiter and Saturn planets consist mainly of hydrogen. The extremely high temperature of the sun and stars enables nuclear fusion of hydrogen atoms liberating large amount of energy.

$$4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + \underset{\text{Positron}}{2\,{}^{0}_{1}e} + \text{Energy}$$

It is the **third most abundant element** on the surface of the earth. On the earth, hydrogen is present in the form of various compounds mainly with oxygen in the form of water and in combination with carbon, nitrogen, sulphur and halogens in the form of organic matter in plants and animal tissues, carbohydrates, proteins, etc. Apart from this, hydrogen is also distributed in the mineral kingdom *e.g.,* in coal, petroleum, oil and natural gas. It constitutes 15.4% of earth's crust and oceans. It is not found in our atmosphere because earth does not have enough gravitational pull to retain light hydrogen molecules.

In the crustal rocks, it is **tenth** in the order of abundance (about 0.15% by weight).

ISOTOPES OF HYDROGEN

Isotopes *are* ***the different forms of the same element which have the same atomic number but different mass numbers.*** Hydrogen has **three isotopes** with mass number 1, 2 and 3 respectively. These are called **protium** (^1_1H), **deuterium** (^2_1H or D) and **tritium** (^3_1H or T). Hydrogen occurring in nature is mainly composed of atoms of protium. It contains only 0.0156% of deuterium mainly in the form of HD. However, the third isotope, tritium is radioactive and emits low energy β-particles (half life of tritium

*Recent studies have shown that hydrogen under very very high pressures is expected to behave as a metal.

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Table 1. Isotopes of hydrogen.

Property	Protium (H)	Deuterium (D)	Tritium (T)
Symbol	$^{1}_{1}H$ or H	$^{2}_{1}H$ or D	$^{3}_{1}H$ or T
Atomic number	1	1	1
Mass number	1	2	3
Relative atomic mass	1.007825	2.014102	3.016049
Nuclear spin quantum number	½	1	½
Radioactive stability	Non-radioactive stable	Non-radioactive stable	Radioactive, emits β-particles ($t_{½}$ = 12.33 *y*)

= 12.33 *y*). Its concentration is about 1 atom per 10^{18} atoms of protium. The symbols, mass numbers, relative abundance and radioactive nature of three isotopes of hydrogen are given in Table 1.

All the three isotopes of hydrogen have one electron in their outer shell and only one proton in the nucleus. However, they differ with respect to the number of neutrons as shown below :

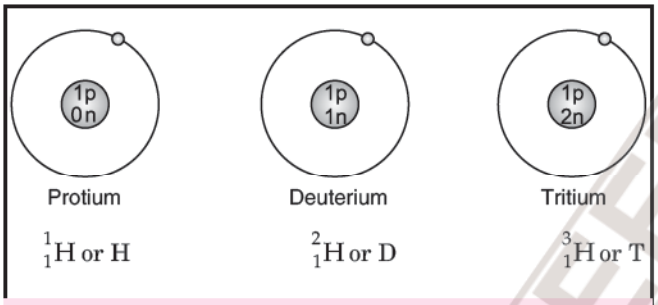

Fig. 2. Isotopes of hydrogen.

A brief description of the isotopes of hydrogen is given below :

***(i)* Protium or ordinary hydrogen** ($^{1}_{1}H$). It is the most common and most abundant isotope of hydrogen. It constitutes 99.985% of the total hydrogen available in nature. The nucleus of hydrogen has one proton and no neutron (mass no. = 1). It is represented as $^{1}_{1}H$ or H. There is a solitary electron outside the nucleus.

***(ii)* Deuterium or heavy hydrogen** ($^{2}_{1}H$ or $^{2}_{1}D$). It constitutes only 0.0156% of the total hydrogen occurring in nature. Its nucleus has one proton and one neutron (mass no. = 2). It is represented as D or $^{2}_{1}H$. It is present in heavy water (D_2O) and can be recovered by fractional electrolysis. It has also one solitary electron outside the nucleus.

***(iii)* Tritium** ($^{3}_{1}H$ or $^{3}_{1}T$). It is the rarest isotope of hydrogen (10^{-15}%) *due to the instability and* **radioactive nature** *of its nucleus*. It is formed in the upper atmosphere by certain nuclear reactions which are induced by cosmic rays. Its nucleus has one proton and two neutrons (mass no. = 3). It is represented as T or $^{3}_{1}H$. It is prepared artificially by the bombardment of nitrogen or an isotope of lithium with deutrons :

$$^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{12}_{6}C + {}^{3}_{1}H \quad (\text{or T})$$

$$^{6}_{3}Li + {}^{1}_{0}n \longrightarrow {}^{4}_{2}He + {}^{3}_{1}H \quad (\text{or T})$$

Thus, *the three isotopes of hydrogen differ only in the number of neutrons in the nucleus.* Since the isotopes have the same atomic number and electronic configuration, they are expected to have similar chemical characteristics.

The common physical properties of H_2, D_2 and T_2 are given in Table 2.

DIHYDROGEN

Preparation of Dihydrogen

Dihydrogen can be prepared by the following methods :

1. By the action of water on metals

Various metals differ in their reactivity towards water. For example,

(*a*) *Very active metals like Na, K and Ca react with water at room temperature evolving dihydrogen.*

Table 2. Physical constants of H_2, D_2 and T_2.

Property	H_2	D_2	T_2
Molecular mass	2.016	4.028	6.03
Melting point (K)	13.96	18.73	20.62
Boiling point (K)	20.39	23.67	25.0
Density (gmL^{-1})	0.09	0.18	0.27
Enthalpy of fusion ($kJ\ mol^{-1}$)	0.117	0.197	0.250
Enthalpy of vaporisation ($kJ\ mol^{-1}$)	0.904	1.226	1.393
Enthalpy of dissociation ($kJ\ mol^{-1}$)	435.88	443.35	446.9
Internuclear distance (pm)	74.14	74.14	—

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$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
$$2K + 2H_2O \longrightarrow 2KOH + H_2$$
$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

The reaction is very vigorous and exothermic so that the hydrogen evolved catches fire. In order to slow down the reaction, amalgam of these metals with mercury are generally used. In the amalgam, only a small surface of the metal is exposed to water and therefore, the reaction is slow.

(*b*) *Less active metals like Zn, Mg, Al,* etc. can liberate hydrogen from water only upon heating.

$$Mg + H_2O \xrightarrow{\text{Heat}} MgO + H_2$$
$$Zn + H_2O \xrightarrow{\text{Heat}} ZnO + H_2$$
$$2Al + 3H_2O \xrightarrow{\text{Heat}} Al_2O_3 + 3H_2$$

(*c*) *Metals like iron and nickel can react only by passing steam since they are very little reactive.*

$$3Fe + 4H_2O(\text{steam}) \xrightarrow{1023-1073K} \underset{\substack{\text{Ferroso-ferric oxide}\\ \text{(Magnetic oxide of iron)}}}{Fe_3O_4} + 4H_2$$

The reaction between iron and steam is used for the large scale preparation of dihydrogen by **Lane's process.**

2. By the electrolysis of water

Dihydrogen of high purity is usually prepared by the electrolysis of using platinum electrodes in the presence of a small amount of acid or alkali. A small quantity of acid or alkali (15-25%) is added to water to make it a good conductor.

$$2H_2O(l) \xrightarrow[\text{traces of acid/base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

During electrolysis, dihydrogen is collected at cathode and dioxygen is liberated at anode. The following reactions take place during the electrolysis of acidulated water :

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode

$$H^+ + e^- \longrightarrow H$$
$$H + H \longrightarrow H_2(g) \uparrow$$

At anode

$$4OH^- - 4e^- \longrightarrow 4OH$$
$$4OH \longrightarrow 2H_2O(l) + O_2(g) \uparrow$$

The hydrogen prepared by this method is of very high purity. However, this method is not commonly used because it is very expensive. This method can be used only at those places where the electricity is cheap.

3. By the action of alkalies on metals

Metals like beryllium, aluminium, zinc and tin react with strong alkalies like NaOH and KOH and liberate dihydrogen.

$$Be + 2NaOH \xrightarrow{\text{Heat}} \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2$$

$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\substack{\text{Sodium}\\ \text{meta-aluminate}}}{2NaAlO_2} + 3H_2$$

$$Sn + 2NaOH + H_2O \longrightarrow \underset{\text{Sodium stannate}}{Na_2SnO_3} + 2H_2$$

$$Zn + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

4. By the action of metals on acids

Active metals like zinc, magnesium and iron which lie above hydrogen in the electrochemical series, can displace dihydrogen from dilute mineral acids such as hydrochloric acid and sulphuric acid. For example,

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$
$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

5. Laboratory preparation of dihydrogen

In the laboratory, dihydrogen can be prepared by the action of dil. H_2SO_4 on granulated zinc.

$$Zn + H_2SO_4(\text{dil.}) \longrightarrow ZnSO_4 + H_2$$

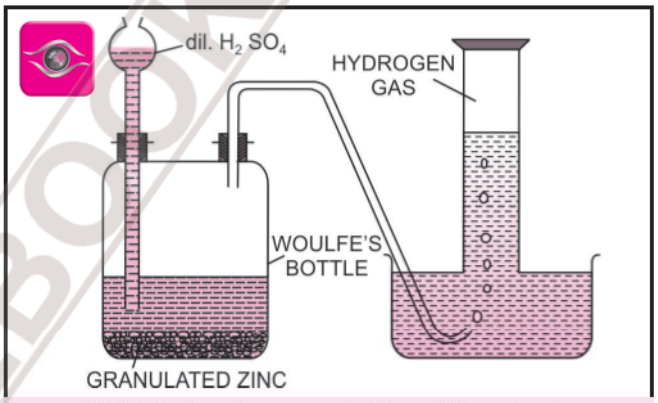

Fig. 3. Laboratory preparation of dihydrogen.

In the preparation of dihydrogen in the laboratory, granulated zinc is taken in a Woulfe's bottle. Dilute sulphuric acid is poured dropwise through thistle funnel on granulated zinc pieces (Fig. 3). The gas evolved is collected over water by the downward displacement of water.

It has been observed that sometimes the bubbles of hydrogen formed stick to the surface of zinc metal and this prevents the further reaction of the acid on the metal. However, this can be prevented by adding a few crystals of copper sulphate to the reaction mixture.

KEY NOTE

The following points should be remembered for the laboratory preparation of dihydrogen :

(*i*) *Pure zinc is not used in the preparation of dihydrogen because its reaction with sulphuric acid is slow. The presence of some impurities increases the rate of reaction due to the formation of electrochemical couples.*

(*ii*) *Concentrated sulphuric acid is also not used for the preparation of dihydrogen because zinc reacts with concentrated acid to form SO_2 gas instead of dihydrogen.*

$$Zn + 2H_2SO_4(\text{conc.}) \longrightarrow ZnSO_4 + SO_2 + 2H_2O$$

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Preparation of Pure Hydrogen

Very pure hydrogen (more than 99.95% purity) may be obtained by the following methods :

(*i*) By the action of pure dil. H_2SO_4 on magnesium ribbon.

$$Mg + H_2SO_4(dil.) \longrightarrow MgSO_4 + H_2$$

(*ii*) By the action of water on sodium hydride.

$$NaH + H_2O \longrightarrow NaOH + H_2$$

(*iii*) By the action of potassium hydroxide on scrap aluminium.

$$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$$

This method is known as **Uyeno's method** and is used for preparing hydrogen for military purposes.

(*iv*) By the electrolysis of warm solution of barium hydroxide [$Ba(OH)_2$] using nickel or platinum electrodes.

Commercial Preparation of Dihydrogen

Commercially dihydrogen is prepared by the following methods :

1. Electrolysis of water. This is the best method for the manufacture of dihydrogen, where electricity is cheap. This has already been discussed (general methods of preparation, 2).

2. By the reaction of steam on coke. Dihydrogen is prepared by passing steam over red hot coke at 1270 K in the presence of Ni as catalyst. In this reaction, first a mixture of CO and dihydrogen is formed.

$$\underset{\text{Coke}}{C(s)} + \underset{\text{Steam}}{H_2O(g)} \xrightarrow[\text{Ni}]{1270\ K} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}} - 121.3\,kJ$$

The mixture of CO and H_2 is called **water gas.** It is an important industrial fuel because it is easy to make and it burns producing a lot of heat. Since the mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is called **synthesis gas** or **syngas**.

The process of producing syngas from coal or coke is called **coal gasification**.

Nowadays, syngas is produced from saw dust sewage, scrap wood, news papers, etc.

> It may be noted that earlier a 1:1 mixture of CO and H_2 was called water gas but now all mixtures of CO and H_2 irrespective of their composition are called syngas.

It is difficult to obtain H_2 from water gas or syngas because CO is difficult to remove. To increase the production of dihydrogen, the mixture of CO and H_2 is mixed with more steam and the gaseous mixture is heated in the presence of iron chromate ($FeCrO_4$) as catalyst at 673 K.

$$\underbrace{H_2 + CO}_{\text{Water gas}} + \underset{\text{Steam}}{H_2O} \xrightarrow[FeCrO_4]{673\ K} CO_2 + 2H_2$$

This chemical reaction in which carbon monoxide of the syngas reacts with steam to form carbon dioxide and more dihydrogen is called **water-gas shift reaction**. The CO_2 thus produced is removed by scrubbing with sodium arsenite solution. Alternatively, the resulting mixture is compressed to about 30 atmospheric pressure and is passed through water. Carbon dioxide dissolves in water under pressure while dihydrogen is released and is collected.

3. Hydrocarbon steam process. Dihydrogen is also prepared by the action of steam on hydrocarbon at high temperatures.

$$C_nH_{2n+2} + nH_2O \xrightarrow{1270\ K} nCO + (2n+1)\,H_2$$

$$e.g., \underset{}{CH_4(g)} + \underset{\text{(steam)}}{H_2O(g)} \xrightarrow{1270\ K} CO(g) + 3H_2(g)$$

$$C_3H_8\,(g) + 3H_2O\,(g) \xrightarrow[\text{Catalyst}]{1270\ K} 3CO(g) + 7H_2\,(g)$$

The CO and H_2 mixture obtained is called syn gas.

Carbon monoxide is oxidised to carbon dioxide by passing the gases and steam over an iron chromate at 673 K resulting in the production of more H_2.

$$CO + H_2O \xrightarrow[673\ K]{FeCrO_4} CO_2 + H_2$$

The CO_2 is removed either by scrubbing the mixture with sodium arsenite or by passing the mixture through water under 30 atm pressure, when CO_2 dissolves leaving behind H_2, which is collected.

The whole process of obtaining dihydrogen from hydrocarbons (or natural gas) is called **steam reforming process**.

4. Lane's process. Hydrogen is prepared by passing alternate currents of steam and water gas over red hot iron. The method consists of two stages :

(*i*) **Oxidation stage.** Super heated steam is passed over iron filings heated to about 1025–1075 K when hydrogen is produced and magnetic oxide of iron (Fe_3O_4) is left behind. This is carried out for half an hour.

$$\underset{\text{Iron filings}}{3Fe} + \underset{\text{(Steam)}}{4H_2O} \xrightarrow{1025-1075\ K} \underset{\text{Magnetic oxide of iron}}{Fe_3O_4} + 4H_2 + 161\ kJ$$

(*ii*) **Reduction stage.** When the whole iron has been oxidised, the supply of steam is stopped and stream of water gas (H_2 + CO) is passed to reduce Fe_3O_4 to iron.

$$Fe_3O_4 + 4\,CO \longrightarrow 3Fe + 4CO_2$$

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

These reactions also take place at 1025–1075K. In actual process, iron is heated in a tube over a furnace maintained at the required temperature and steam and water gas are passed over it alternately.

5. From methanol. Relatively small quantities of dihydrogen are obtained by passing a 1 : 1 molar mixture of vaporised methanol and water over a special type of catalyst ***'base metal chromite type'*** at 673 K. The mixture of dihydrogen and carbon monoxide obtained is made to react with steam to give CO_2 and more dihydrogen.

$$CH_3OH \xrightarrow[\text{Catalyst}]{673\ K} CO + 2H_2$$

$$CO + H_2O \xrightarrow[\text{Catalyst}]{673\ K} CO_2 + H_2$$

6. By-product in the manufacture of caustic soda. Dihydrogen is also produced as a by-product of the brine electrolysis process for the manufacture of sodium hydroxide and chlorine.

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During electrolysis, the following reactions take place :

at anode : $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

at cathode : $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

Overall reaction

$2Cl^-(aq) + 2H_2O(l) \longrightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$

or $2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l)$

$\longrightarrow Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$

(adding Na^+ ions on both sides)

Presently about 77% of the industrial hydrogen produced is from petrochemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

Properties of Dihydrogen

Physical properties

The important physical properties of dihydrogen are :

(*i*) It is a *colourless, tasteless* and *odourless* gas.

(*ii*) It is slightly soluble in water.

(*iii*) It is highly combustible and therefore should be handled carefully.

(*iv*) It is lightest substance known. For example, one litre of hydrogen at N.T.P. weighs only 0.0899 g.

(*v*) Its density is about 1/14th of that of air.

The physical constants of atomic and molecular hydrogen are given in Table 3.

It may be noted that the term *dihydrogen* is used for H_2 molecule while referring to the isotopic mixture with natural abundance for H and D. However, in terms of isotopes, the correct term for H_2 is **diprotium.** Similarly, H^+ is named as **proton** and **hydron** is used in relation to isotopic mixture.

Chemical properties

Dihydrogen is quite stable and dissociates into hydrogen atoms only when heated above 2000 K.

$$H_2(g) \xrightarrow{2000\ K} H(g) + H(g)$$

Above 2000K, the dissociation of hydrogen into atoms is only 0.081% which increases to 95.5% at 5000 K.

Its bond dissociation energy is very high.

$$H_2 \longrightarrow H + H;\quad \Delta H = 435.9\ kJ\ mol^{-1}$$

The H—H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. Due to its high bond dissociation enthalpy, it is not very reactive. However, it combines with many elements or compounds.

1. Action with metals. Dihydrogen combines with metals like sodium, potassium and calcium upon heating to form corresponding hydrides which are of ionic nature (salt-like). For example,

$$2M(s) + H_2(g) \longrightarrow 2MH(s)$$

(M = alkali metal)

e.g., $2Na + H_2 \xrightarrow{Heat} \underset{\text{Sodium hydride}}{2NaH}$

$Ca + H_2 \xrightarrow{Heat} \underset{\text{Calcium hydride}}{CaH_2}$

With transition metals (elements of *d*-block) such as platinum, palladium, nickel, etc. dihydrogen forms **interstitial hydrides** in which the small molecules of dihydrogen occupy the interstitial sites in the crystal lattices of these hydrides. As a result of formation of interstitial hydrides, these metals adsorb large volume of hydrogen on their surface. This property of adsorption of a gas by a metal is called **occlusion**. The occluded hydrogen can be liberated from the metals by strong heating.

2. Reaction with non-metals. Dihydrogen reacts with non-metals under specific conditions. Some of the reactions are summed up below :

Dioxygen $\quad 2H_2(g) + O_2(g) \xrightarrow[\text{or electric discharge}]{970K} \underset{\text{Water}}{2H_2O(l)}$

This reaction is strongly exothermic ($\Delta H = -285.9\ kJ\ mol^{-1}$)

Dinitrogen $\quad N_2(g) + 3H_2(g) \xrightarrow[673\,K,\ 200\ atm]{Fe,\ Mo} \underset{\text{Ammonia}}{2NH_3}$

This reaction is also exothermic ($\Delta H = -92.6\ kJmol^{-1}$). Here Fe acts as a catalyst and Mo acts as a promoter.

This reaction is the basis for the **manufacture of ammonia by the Haber process.**

Halogens

$H_2 + F_2 \xrightarrow{Dark} 2HF$

$H_2 + Cl_2 \xrightarrow{Diffused\ sunlight} 2HCl$

$H_2 + Br_2 \xrightarrow{673K,\ pressure} 2HBr$

$H_2 + I_2 \xrightarrow{673\ K,\ Pt} 2HI$

In general,

$H_2(g) + X_2(g) \longrightarrow 2HX(g)$

(X = F, Cl, Br, I)

Table 3. Physical constants of atomic and molecular hydrogen.

Atomic properties		Molecular properties	
Atomic radius (pm)	= 37	Melting point (K)	= 13.8
Ionic radius of H^- ion (pm)	= 210	Boiling point (K)	= 20.4
Ionisation enthalpy ($kJ\ mol^{-1}$)	= 1312	Density ($g\ cm^{-3}$)	= 0.0899
Electron affinity ($kJ\ mol^{-1}$)	= 72.8	Bond length (pm)	= 74.2
Electronegativity	= 2.1	Bond dissociation Enthalpy ($kJ\ mol^{-1}$)	= 435.9

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The reactivity of halogen towards dihydrogen decreases as :

$$F_2 > Cl_2 > Br_2 > I_2$$

As a result, fluorine reacts in dark, chlorine in the presence of sunlight, bromine reacts only upon heating while the reaction with iodine occurs in the presence of a catalyst.

Sulphur $H_2 + S \xrightarrow{700\ K} H_2S$

Carbon $C + 2H_2 \xrightarrow{1375\ K} \underset{\text{Methane}}{CH_4}$

$2C + H_2 \xrightarrow[\text{Electric spark}]{2775\ K} \underset{\text{Acetylene}}{C_2H_2}$

3. Reaction with metal oxides. Dihydrogen acts as a strong reducing agent and therefore, it reduces oxides of metals (less active than iron) to metals.

$$M_xO_y(s) + yH_2(g) \longrightarrow xM(s) + yH_2O(l)$$

For example,

$CuO + H_2 \xrightarrow{Heat} \underset{\text{Copper}}{Cu} + H_2O$

$ZnO + H_2 \xrightarrow{Heat} \underset{\text{Zinc}}{Zn} + H_2O$

$PbO + H_2 \longrightarrow \underset{\text{Lead}}{Pb} + H_2O$

$Fe_3O_4 + 4H_2 \xrightarrow{Heat} \underset{\text{Iron}}{3Fe} + 4H_2O$

It may be ***noted*** *that the oxides of strongly electropositive metals as those of alkali and alkaline earth metals are not reduced by this method.*

Dihydrogen also reduces some metal ions in aqueous solution. For example,

$$Pd^{2+}(aq) + H_2(g) \longrightarrow Pd(s) + 2H^+(aq)$$

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

4. Reaction with carbon monoxide Dihydrogen reacts with CO at 700 K in the presence of a catalyst ZnO/Cr_2O_3 to form methanol.

$$CO + H_2 \xrightarrow[ZnO,\ Cr_2O_3]{700\ K,\ 200\ atm} \underset{\text{Methanol}}{CH_3OH}$$

5. Reaction with unsaturated hydro-carbons. Dihydrogen reacts with unsaturated hydrocarbons such as ethylene and acetylene to give saturated hydrocarbons.

$\underset{\text{Ethylene}}{H_2C = CH_2} + H_2 \xrightarrow[473\ K]{Ni \text{ or } Pt \text{ or } Pd} \underset{\text{Ethane}}{H_3C - CH_3}$

$\underset{\text{Acetylene}}{HC \equiv CH} + 2H_2 \xrightarrow[473\ K]{Ni \text{ or } Pt \text{ or } Pd} \underset{\text{Ethane}}{H_3C{-}CH_3}$

The hydrogenation of many organic compounds using homogeneous and heterogeneous catalysis constitute important industrial processes. For example :

(*i*) **Hydroformylation of olefins to aldehydes**. Olefins react with carbon monoxide and dihydrogen in the presence of octacarbonyl dicobalt $[Co(CO)_4]_2$ as catalyst under high temperature and pressure to form aldehydes.

$$\underset{\text{Olefin}}{RCH = CH_2} + H_2 + CO \xrightarrow[\text{high temp. and pressure}]{[Co(CO)_4]_2} \underset{\text{Aldehyde}}{RCH_2CH_2CHO}$$

This reaction is called **hydroformylation** or **oxo process**. The aldehyde thus formed is further reduced to alcohol by the reaction :

$$\underset{\text{Aldehyde}}{RCH_2CH_2CHO} + H_2 \longrightarrow \underset{\text{Alcohol}}{RCH_2CH_2CH_2OH}$$

(*ii*) **Aldehyde Hydrogenation of oils**. The hydrogenation of vegetable oils which are polyunsaturated give solid edible fats (margarine and vanaspati).

This reaction is used in the **hydrogenation or hardening of oils.** The vegetable oils such as groundnut oil or cotton-seed oil are poly-unsaturated in nature because they contain double bonds in their molecules. The C = C bonds in oils can easily undergo oxidation and the oil becomes **rancid** *i.e.,* unpleasant in taste. Hydrogenation reduces the number of double bonds but does not completely eliminate them. Under controlled conditions, dihydrogen is passed through the oils at about 473 K in the presence of nickel catalyst to form solid fats.

$\underset{\text{(liquid)}}{\text{Vegetable oil}} + H_2 \xrightarrow[473\ K]{Ni} \underset{\text{(solid)}}{\text{Fat}}$

Edible oils and margarine can be prepared by hydrogenation of vegetable oils like soyabean, corn, cotton seed oils etc. The vanaspati ghee such as *Dalda, Rath* etc. are usually prepared on a large scale in India by this process.

Uses of Dihydrogen

(*i*) It is used as a reducing agent in the laboratory and industry. In metallurgical processes, it is used to reduce heavy metal oxides to metals.

(*ii*) It is used in the manufacture of vanaspati fat by the hydrogenation of poly-unsaturated vegetable oils like soyabean, cotton seeds etc.

(*iii*) The most important use of dihydrogen is in the manufacture of ammonia by Haber process.

$$N_2(g) + 3H_2 \underset{\text{Catalyst}}{\overset{673K,\ 200\ atm}{\rightleftharpoons}} 2NH_3(g)$$

(*iv*) It is used in the preparation of many compounds such as metal hydrides, hydrogen chloride, water gas, methanol and fertilizers such as urea, ammonium sulphate, etc.

(*v*) Dihydrogen is used in the manufacture of bulk organic chemicals such as methanol.

$$CO(g) + 2H_2 \xrightarrow[700\ K,\ 200\ atm]{Cobalt\ catalyst} CH_3OH(l)$$

(*vi*) It is used as a rocket fuel for space research in the form of liquid hydrogen and liquid oxygen.

(*vii*) It is used in the manufacture of synthetic petrol.

(*viii*) It is used in the *atomic hydrogen* torch and *oxy hydrogen torches* for cutting and welding. Dihydrogen is dissociated with the help of an electric arc and the hydrogen atoms produced are allowed to recombine on the surface to be welded. High temperature of about 4000 K is generated.

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(*ix*) Dihydrogen is also used in bubble chambers as liquid hydrogen for the study of high energy particles.

(*x*) Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over conventional fossil fuels and electric power. It does not produce any pollution and releases larger energy per unit mass of fuel in comparison to gasoline and other fuels.

Learning Plus

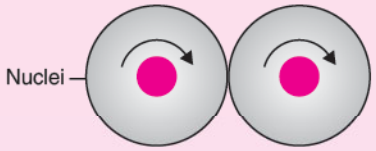
ORTHO AND PARA HYDROGEN

A molecule of dihydrogen contains two atoms. The nuclei of both the atoms in each molecule of dihydrogen are spinning. Depending upon the direction of the spin of the nuclei, the hydrogens are of two types :

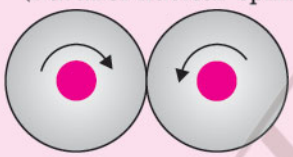
(*a*) *Molecules of hydrogen in which the spins of both the nuclei are in the same directions (parallel nuclear spins)* are called **ortho hydrogen.**

(*b*) *Molecules of hydrogen in which the spins of both the nuclei are in the opposite directions* (anti-parallel nuclear spins) are called **para hydrogen.**

These two types of hydrogens are called **nuclear spin isomers** and are shown below :



Ortho hydrogen
(Parallel nuclear spins)



Para hydrogen
(Antiparallel nuclear spins)

These two isomers have 1 and 0 nuclear spin respectively. The conversion of one isomer into another isomer is a slow process. Ordinary dihydrogen is an equilibrium mixture of ortho and para hydrogen.

$$\text{Ortho hydrogen} \rightleftharpoons \text{Para hydrogen}$$

The amount of ortho and para hydrogen varies with temperature. The ratio of ortho to para hydrogen increases with increase in temperature upto a temperature of about 300 K and thereafter it becomes almost constant. It has been observed :

(*i*) At 0K, hydrogen contains mainly para hydrogen which is more stable.

(*ii*) At the temperature of liquefaction of air, the ratio of ortho and para hydrogen is 1 : 1.

(*iii*) At the room temperature (300 K), the ratio of ortho to para hydrogen is 3 : 1.

(*iv*) Even at very high temperatures, the ratio of ortho to para hydrogen can never be more than 3 : 1.

Thus, **it has been possible to get pure para hydrogen by cooling ordinary hydrogen gas to a very low temperature (close to 20 K) but it is never possible to get a sample of hydrogen containing more than 75% of ortho hydrogen.**

The physical properties of dihydrogen are not affected significantly by nuclear spin isomerism. However, some of the following are some notable differences :

(*i*) The thermal conductivity of para-hydrogen is about 50% greater than that of ortho-hydrogen, and

(*ii*) The melting point of para hydrogen is 0.15 K below that of hydrogen containing 75% ortho hydrogen.

Learning Plus

ATOMIC HYDROGEN

Atomic hydrogen. The hydrogen obtained by the dissociation of hydrogen molecules is called **atomic hydrogen.** Because of high H—H bond enthalpy, atomic hydrogen is produced only at a high temperature in an electric arc or under ultraviolet radiations.

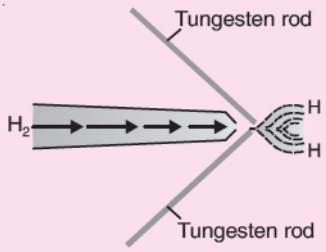
It is obtained by passing dihydrogen gas at atmospheric pressure through an electric arc struck between two tungsten rods.

The electric arc maintains a temperature around 4000 – 4500°C. As the molecules of dihydrogen gas pass through the electric arc, these absorb energy and get dissociated into atoms as

$$H_2(g) \xrightarrow[\text{arc}]{\text{Electric}} 2H(g) : \Delta H = 435.90 \text{ kJ mol}^{-1}$$

The atomic hydrogen is stable only for a fraction of a second and is extremely reactive. The life time of atomic hydrogen is 0.3 sec and therefore, it immediately gets converted into the molecular form liberating a large amount of energy which is used for cutting and welding purposes.

This arrangement is also called **atomic hydrogen torch.**



ATOMIC HYDROGEN TORCH

Since the atomic orbital of hydrogen is incomplete with $1s^1$ electronic configuration, it needs only one electron to achieve stable noble gas configuration. Therefore, *atomic hydrogen is very reactive and combines with almost all elements.* It reacts in three different ways:
(*i*) by loss of its only one electron to form H^+.
(*ii*) by gain of one electron to form H^- and
(*iii*) by sharing its electron with other atoms to form single covalent bond.

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Practice Problems

1. Which isotope of hydrogen
   (*i*) does not contain neutron
   (*ii*) is radioactive ?
2. Which gaseous compound on treatment with dihydrogen produces methanol ?
3. Why is dihydrogen not preferred in balloons these days ?
4. Which of the following metals can be used for liberating hydrogen from dilute hydrochloric acid?
   (*i*) Zinc (*ii*) Copper (*iii*) Iron (*iv*) Silver (*v*) Magnesium
5. Name the constituents of water gas.
6. Name one industrial method for the preparation of dihydrogen.
7. Arrange H_2, D_2 and T_2 in the decreasing order of their
   (*i*) boiling points (*ii*) heat of fusion
8. Name the products obtained when hydrogen reacts under suitable conditions with
   (*i*) Nitrogen (*ii*) Carbon monoxide (*iii*) Lead oxide
9. Does hydrogen support combustion ?
10. Name one compound each in which hydrogen exists in (*i*) positive oxidation state, and (*ii*) negative oxidation state.

Answers to Practice Problems

1. (*i*) Protium (*ii*) Tritium
2. Carbon monoxide
3. Because it is combustible in nature.
4. (*i*), (*iii*) and (*v*)
5. Carbon monoxide and hydrogen.
6. Bosch process.
7. (*i*) $T_2 > D_2 > H_2$ (*ii*) $T_2 > D_2 > H_2$
8. (*i*) Ammonia (*ii*) Methanol (*iii*) Lead
9. No, it does not support combustion.
10. (*i*) HCl (*ii*) NaH

HYDRIDES

Hydrogen under certain conditions combines with almost all elements, metals and non-metals (except noble gases). ***The binary compounds of hydrogen with other elements*** are called **hydrides.** These hydrides have the formula EH_x (*e.g.,* MgH_2) or E_mH_n (*e.g.,* B_2H_6) and are formed by

(*i*) all main group elements except the noble gases and probably indium and thallium

(*ii*) all lanthanoids and actinoids

(*iii*) transition elements such as Sc, Y, La, Ac, Tc, Zr, Hf and to lesser extent V, Nb, Ta, Cr, Cu and Zn. Among the transition metals, palladium hydride has been extensively studied.

The hydrides are classified into three main types :

1. *Ionic or salt like or saline hydrides*
2. *Covalent or molecular hydrides*
3. *Metallic or interstitial hydrides.*

1. Ionic hydrides or saline hydrides

These are formed by the combination of hydrogen with metals which are highly electropositive in character. These include elements of *s*-block elements *i.e.* of group 1 (alkali metals), group 2 (alkaline earth metals with the exception of Be and Mg) as well as some other elements such as lanthanum.

These are formed by the transfer of electrons from metals to hydrogen atom and contain hydrogen as H^- ion. For example, lithium hydride (Li^+H^-), sodium hydride (Na^+H^-), calcium hydride ($Ca^{2+}H_2^-$), etc.

Ionic hydrides are prepared by the direct combination of the metals with hydrogen at high temperatures usually close to 1025 K.

$$\underset{\text{(Molten)}}{2Li} + H_2 \longrightarrow 2LiH$$

$$2K + H_2 \xrightarrow{673\ K} 2KH$$

$$Ca + H_2 \xrightarrow{1073\ K} CaH_2$$

$$Sr + H_2 \xrightarrow{1123\ K} SrH_2$$

General Characteristics of Ionic Hydrides

The general characteristics of ionic hydrides are given below :

1. Ionic hydrides are generally white or light grey non-volatile and non-conducting crystalline solids. They behave like salts and are also referred to *salt like hydrides.* However, *BeH_2 and MgH_2 have covalent polymeric structures.*
2. They have high melting and boiling points.
3. The binary hydrides of alkali metals (LiH, NaH, KH, RbH and CsH) have rock salt like structure.
4. They conduct electricity in fused state liberating hydrogen at the anode. The negative charge on the hydrogen in these hydrides is proved by electrolysis of molten lithium hydride at 973 K. During electrolysis, lithium metal deposits at the cathode and hydrogen is liberated at the anode.

$$LiH \underset{973\ K}{\rightleftharpoons} Li^+ + H^-$$

At cathode :

$$Li^+ + e^- \longrightarrow \underset{\text{(deposited)}}{Li}$$

At anode :

$$H^- - e^- \longrightarrow H$$

$$H + H \longrightarrow H_2\uparrow$$

This shows the existence of the hydride (H^-) ion.

$$2H^-(melt) \longrightarrow H_2(g) + 2e^-$$

5. Their densities are higher than those of metals.
6. LiH, CaH_2 and SrH_2 are the most stable hydrides of this class, others undergo thermal decomposition above 775 K. Enthalpies of formation of hydrides of group 1 and 2 are given in Table 4. These values give the relative stabilities of these hydrides. *Larger the enthalpies of formation, greater are their stabilities.*

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Table 4. Enthalpies of formation of hydrides of group 1 and 2.

Hydride	Enthalpies of formation ($kJ\ mol^{-1}$)	Temperature of dissociation (K)
	Group 1	
LiH	90.3	823
NaH	58.1	483
KH	58.9	473
RbH	56.5	443
CsH	54.4	443
	Group 2	
CaH_2	188.7	1158 K
SrH_2	176.9	858 K
BaH_2	171.1	503 K

The thermal stability of the alkali metal hydrides decreases from LiH to CsH.

$$LiH > NaH > KH > RbH > CsH$$

The order of stability in alkaline earth metal hydrides is :

$$CaH_2 > SrH_2 > BaH_2$$

7. The ionic hydrides are oxidised by air to form metal oxide and water.

$$2EH + O_2 \longrightarrow E_2O + H_2O$$

RbH and CsH burn spontaneously at room temperature whereas LiH is unreactive at moderate temperatures.

8. They are hydrolysed by water with the formation of hydroxide and liberation of hydrogen.

$$LiH + H_2O \longrightarrow LiOH + H_2$$
$$NaH + H_2O \longrightarrow NaOH + H_2$$

Therefore, their aqueous solutions are **basic.**

Facts More interesting facts

1 Proton H^+ has very small size (about 10^{-15} m radius) and intense electric field. It binds to a water molecule to form hydrated proton or hydronium ion H_3O^+. This species has been detected in many compounds such as $H_3O^+Cl^-$ in the solid state. In aqueous solution, hydronium ion is itself strongly hydrated in solution to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$.

1 Heavy hydrogen or deuterium (D_2) was separated from liquid hydrogen by fractional evaporation by Harold C. Urey. For his contribution, Urey was awarded Noble Prize in Chemistry in 1934.

The reaction of these hydrides with water is very **explosive.** The fires so produced cannot be extinguished by carbon dioxide because it gets reduced by the hot metal hydride. To extinguish the fire, only sand can be used because it is a solid.

9. They react with protonic solvents liberating hydrogen.

$$LiH + CH_3OH \longrightarrow LiOCH_3 + H_2\uparrow$$
$$NaH + NH_3 \longrightarrow NaNH_2 + H_2\uparrow$$

10. They act as powerful reducing agents, especially at high temperatures. For example,
NaH reduces CO and CO_2 to formates on heating.

$$2CO + NaH \xrightarrow{Heat} HCOONa + C$$

$$CO_2 + NaH \xrightarrow{Heat} \underset{\text{Sodium formate}}{HCOONa}$$

They reduce sulphates to sulphides

$$PbSO_4 + 2CaH_2 \longrightarrow PbS + 2Ca(OH)_2$$

They also reduce some halides and oxides as :

$$Fe_3O_4 + 4NaH \xrightarrow{Heat} 3Fe + 4NaOH$$
$$SiCl_4 + 4NaH \longrightarrow SiH_4 + 4NaCl$$
$$2BF_3 + 6NaH \xrightarrow{450K} \underset{\text{Diborane}}{B_2H_6} + 6NaF$$

They are capable of reducing organic acids to alcohols.

$$RCOOH + 2LiH \longrightarrow RCH_2OH + Li_2O$$

11. Some hydrides are used to prepare complex hydrides of other metals. The complex hydrides also act as reducing agents. For example,
LiH reacts with aluminium chloride in ether solution or diborane to form lithium aluminium hydride, $LiAlH_4$ (complex hydride) or lithium borohydride ($LiBH_4$).

$$8LiH + Al_2Cl_6 \longrightarrow \underset{\text{Lithium aluminium hydride}}{2LiAlH_4} + 6LiCl$$

$$2LiH + \underset{\text{Diborane}}{B_2H_6} \xrightarrow{\text{Dry ether}} \underset{\text{Lithium borohydride}}{2LiBH_4}$$

NaH reacts with diborane (B_2H_6) to form sodium borohydride as :

$$2NaH + B_2H_6 \xrightarrow{Ether} \underset{\text{Sodium borohydride}}{2NaBH_4}$$

The hydrides of lanthanides are also regarded as ionic hydrides. However, there is some doubt about their true ionic character. Their heats of formation are quite high suggesting ionic character but these are non-stoichiometric like metallic hydrides (discussed later on).

Uses of Ionic Hydrides

The ionic hydrides and their complexes ($LiAlH_4$, $LiBH_4$, $NaBH_4$, etc.) are used as reducing agents. Since they evolve hydrogen when heated and, therefore, ignite spontaneously, and are used as solid fuels.

2. Molecular or covalent hydrides

These hydrides are formed by the combination of elements of comparatively higher electronegativity

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as of p-block elements. The common elements forming molecular hydrides are B, C, N, O, F, Si, P, S, Cl, Ga, Ge, As, Se, Br, In, Sn, Pb, Te, I, Tl, Pb, At, etc. The bonds formed are mostly covalent in character. But in some cases, as for example in HF, the bond may be partly ionic in character as well. These hydrides, therefore, have *molecular lattices.* The molecules are held together by weak van der Waals forces. In some cases, hydrogen bonds are also formed. In many cases but not in all cases, the general formula for covalent hydrides is EH_{8-n} where E stands for the symbol of a metal and *n* is the group number.

The systematic names of these hydrides are usually formed from the name of the element and the suffix ***–ane***. For example, phosphane (PH_3), silane (SiH_4), germane (GeH_4), etc. However, these are popularly known by their common names such as phosphine (PH_3), water (H_2O), ammonia (NH_3), etc. It may be noted that according to systematic nomenclature water should be named as oxidane, ammonia as azane, etc. However, the scientists are reluctant to use these systematic names which are popularly known for such a long time in chemistry.

Preparation of Covalent Hydrides

Covalent hydrides are prepared by the following methods :

(*i*) By direct combination of elements, *e.g.*,

$$H_2 + F_2 \xrightarrow{23K} 2HF$$

$$2H_2 + O_2 \xrightarrow{\text{Electric discharge}} 2H_2O$$

$$3H_2 + N_2 \xrightarrow[673K,\ 200\ atm]{Fe,\ Mo} 2NH_3$$

(*ii*) By hydrolysis of metal borides, carbides, nitrides, phosphides, etc.

$$Mg_3B_2 + 6H_2O \longrightarrow \underset{\text{Diborane}}{3Mg(OH)_2 + B_2H_6}$$

$$Ca_3P_2 + 6H_2O \longrightarrow \underset{\text{Phosphine}}{3Ca(OH)_2 + 2PH_3}$$

$$Mg_3N_2 + 6H_2O \longrightarrow \underset{\text{Ammonia}}{3Mg(OH)_2 + 2NH_3}$$

$$Al_4C_3 + 12H_2O \longrightarrow \underset{\text{Methane}}{4Al(OH)_3 + 3CH_4}$$

(*iii*) By the action of acids on suitable binary compounds :

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 12HCl \longrightarrow \underset{\text{Methane}}{3CH_4} + 4AlCl_3$$

$$\underset{\text{Magnesium boride}}{2Mg_3B_2} + 4H_3PO_4 \longrightarrow \underset{\text{Tetraborane}}{B_4H_{10}} + 2Mg_3(PO_4)_2 + H_2$$

$$\underset{\text{Iron sulphide}}{FeS} + H_2SO_4 \longrightarrow \underset{\text{Hydrogen sulphide}}{H_2S} + FeSO_4$$

$$\underset{\text{Calcium phosphide}}{Ca_3P_2} + 3H_2SO_4 \longrightarrow \underset{\text{Phosphine}}{2PH_3} + 3CaSO_4$$

(*iv*) By reduction of certain compounds with suitable reducing agents like $LiAlH_4$, $NaBH_4$ (in ether solution).

$$4BCl_3 + 3LiAlH_4 \longrightarrow \underset{\text{Diborane}}{2B_2H_6} + 3AlCl_3 + 3LiCl$$

$$SiCl_4 + LiAlH_4 \longrightarrow \underset{\text{Silane}}{SiH_4} + AlCl_3 + LiCl$$

$$SnCl_4 + LiAlH_4 \xrightarrow{\text{Ether}} LiCl + AlCl_3 + \underset{\text{Stannane}}{SnH_4}$$

$$GeCl_4 + LiAlH_4 \xrightarrow{\text{Ether}} LiCl + AlCl_3 + \underset{\text{Germane}}{GeH_4}$$

$$4H_3AsO_3 + 3NaBH_4 \longrightarrow 4AsH_3 + 3H_3BO_3 + 3NaOH$$

General Characteristics of Covalent Hydrides

Some important general characteristics of molecular hydrides are discussed below :

1. The molecular hydrides are soft.
2. They have low melting and boiling points and, are generally, volatile in nature.
3. They have low electrical conductivity.
4. The properties of the covalent hydrides depend upon the electronegativity difference between hydrogen and the atom bonded to it. For example, the hydrides become increasingly acidic in character on moving from left to right along a given row in the periodic table. Thus, while NH_3 is weak base, H_2O is neutral and HF is acidic. Similarly, in the next row while PH_3 is a weak base, H_2S is a weak acid and HCl is highly acidic.

Molecular hydrides are further classified according to the relative number of electrons and bonds in their Lewis structures. These are *electron deficient, electron precise* and *electron rich molecular hydrides.*

(*i*) **Electron deficient molecular hydrides.** These have less electrons for writing their conventional Lewis structures. For example, the hydrides of group 13 are electron deficient compounds and exist in polymerised forms such as B_2H_6 (diborane), $(AlH_3)_n$, etc.

(*ii*) **Electron precise molecular hydrides.** These have sufficient number of electrons required for their conventional Lewis structures. For example, the hydrides formed by group 14 elements are electron precise molecular hydrides such as CH_4. It has tetrahedral structure.

(*iii*) **Electron rich molecular hydrides.** These have excess electrons as required by conventional Lewis structures. The excess electrons are present as lone pairs of electrons. The hydrides of group 15–17 form such compounds. For example, water has two and ammonia has one lone pair of electrons.

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The presence of lone pairs on the highly electronegative atoms like nitrogen, oxygen and fluorine result in the formation of hydrogen bonds in these molecular hydrides. Because of the hydrogen bonds in these molecules, they exist as associated molecules such as $(NH_3)_n$, $(H_2O)_n$, $(HF)_n$, etc. As a result of aggregation, they have abnormally high boiling points and high permittivities. For example, NH_3, H_2O and HF have abnormally high boiling points as compared to the boiling points of hydrides of each group (*i.e.,* PH_3, H_2S and HCl).

3. Metallic or Interstitial Hydrides

Most of the *d*-block elements (*i.e.,* transition elements) and *f*-block elements form metallic hydrides on reacting with hydrogen. Among the *d*-block elements, the metallic hydrides of groups 3, 4 and 5 are very common. In group 6, chromium alone forms CrH. The metals of groups 7, 8 and 9 do not form hydrides. This region of periodic table from group 7 to 9 is referred to as the **hydride gap.** The common examples of hydrides of groups 3 to 5 are :

ScH_2, YH_2, YH_3, LaH_2, LaH_3, TiH_2, ZrH_2, HfH_2, VH, VH_2, NbH, NbH_2, TaH. The *f*-block elements form hydrides of limiting compositions of EH_2 and EH_3.

Beryllium and magnesium of *s*-block elements also form metallic hydrides. In these hydrides, hydrogen exists in the atomic rather than ionic form. These are interstitial compounds as the hydrogen atoms occupy interstitial positions in the metal lattices. This is due to small size of hydrogen atoms compared to the metal atoms. Some workers regard them nearly as solid solutions.

These are prepared by adsorbing hydrogen directly at appropriate temperatures into the interstices of transition metal lattices. For example, palladium metal adsorbs hydrogen to form palladium hydride. In some cases, the metals are used as cathodes in the electrolysis of their aqueous solutions so that they adsorb hydrogen during electrolysis. PdH_2 is prepared by this method.

General Characteristics of Metallic Hydrides

1. They are hard, have a metallic lustre, conduct electricity and have significant magnetic properties.

2. The densities of these hydrides are lower than those of metals from which they are formed because the crystal lattice expands due to inclusion of H_2.

3. These compounds are non-stoichiometric, and their composition varies with temperature and pressure. The compositions of hydrides of titanium and zirconium, for example, are represented by TiH_x (x = 1.5 to 1.8) and ZrH_x (x = 1.30 to 1.75), respectively. Some other examples are NiH_x (x = 0.6–0.7), PdH_x (x = 0.6 – 0.8), $VH_{0.56}$, etc. The density of each compound is less than that of the metal itself and the properties are not much different from that of the metal.

4. They give out hydrogen easily and are strong reducing agents. This suggests that hydrogen is present in the atomic state. These compounds are used as industrial reducing agents.

The *f*-block elements (*i.e.,* lanthanoids and actinoids) also form non–stoichiometric interstitial hydrides, *e.g.*, $LaH_{2.87}$, $YbH_{2.55}$, $CeH_{2.69}$, $TbH_{3.07}$. These hydrides have lower densities than their respective metals.

Metallic hydrides can be used as hydrogen storage media. This property has potential for hydrogen storage and as a source of energy for vehicles.

The characteristics of different hydrides are listed in Table 5.

Table 5. Characteristics of different hydrides.

Type	Physical character	Bonding	Examples
Ionic	Salt like solids, good conductors in fused state	Largely ionic	LiH, NaH, CaH_2
Molecular or covalent	Gaseous or volatile liquids, non-conductors	Covalent	HF, H_2O, CH_4, H_2S
Metallic or interstitial	Metallic appearance brittle, conductors, semiconductors	Partly ionic and metallic bond	$ZrH_{1.9}$, $TiH_{1.73}$, $LaH_{2.76}$

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Learning Plus

Polymeric Hydrides or Complex Hydrides

In addition to above three main types of hydrides, some hydrides are regarded as ***polymeric hydrides*** and ***complex hydrides***. These are briefly discussed below :

(*i*) **Polymeric hydrides.** These are formed by elements having electronegativity range between 1.4 and 2.0. These hydrides consist of molecules held together in two or three dimensions by hydrogen bridges. These are generally solids. The common examples of polymeric hydrides are $(BeH_2)_n$, $(MgH_2)_n$, $(AlH_3)_n$, $(InH_3)_n$, $(SiH_4)_n$, etc. The preparation and properties of beryllium hydride are discussed below :

Preparation. It was first prepared by the reduction of $BeCl_2$ with LiH.

$$BeCl_2 + 2LiH \longrightarrow BeH_2 + 2LiCl$$

It can also be prepared by heating tertiary butyl beryllium at 100°C.

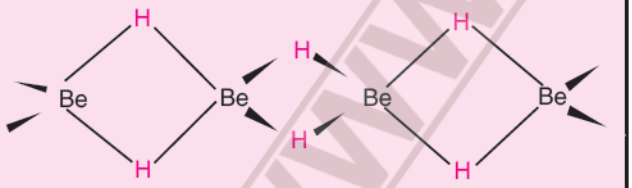
$$Be[(CH_3)_3C]_2 \xrightarrow{373\,K} BeH_2 + \underset{\text{Isobutylene}}{2(CH_3)_2C = CH_2}$$

Properties. (*i*) It is amorphous white solid. It is stable upto 250°C and when heated above 250°C, it begins to evolve hydrogen gas.

(*ii*) It is moderately stable in air or water but it is rapidly hydrolysed by acids giving H_2.

$$BeH_2 + 2HCl \longrightarrow BeCl_2 + 2H_2$$

Structure. BeH_2 appears to be highly polymerised by means of BeHBe, three centre bonds as shown below :



(*ii*) **Complex hydrides.** These are the compounds which contain hydride ions co-ordinated to metal ions. These are common in both the transition and non-transition metals. The most common examples of complex hydrides are formed by the elements of group IIIA such as B, Al, Ga, etc. For example, lithium aluminium hydride ($LiAlH_4$), sodium and lithium borohydrides ($LiBH_4$, $NaBH_4$), etc. These are briefly discussed below :

Lithium aluminium hydride

Preparation. It is prepared by reacting lithium hydride with anhydrous aluminium chloride in ether.

$$\underset{\text{(anhydrous)}}{4LiH + AlCl_3} \xrightarrow{\text{Ether}} LiAlH_4 + 3LiCl$$

On an industrial scale, it is prepared by direct combination of constituent elements under high pressure in the presence of ether.

$$Li + Al + 2H_2 \xrightarrow[350\text{ atm.}]{413\,K} LiAlH_4$$

Properties. (*i*) It is a white, non-volatile crystalline solid which is freely soluble in ethers. It is stable upto 120°C.

(*ii*) It decomposes on heating liberating hydrogen.

$$2LiAlH_4 \xrightarrow{\text{Heat}} 2LiH + 2Al + 3H_2$$

(*iii*) It is readily attacked by water and ethanol giving hydrogen gas

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 2H_2$$

$$LiAlH_4 + 3C_2H_5OH \longrightarrow Li[AlH(OC_2H_5)_3] + 3H_2$$

(*iv*) It reduces compounds of boron, aluminium, silicon, tin, etc. to form hydrides.

$$SiCl_4 + LiAlH_4 \xrightarrow{\text{Ether}} SiH_4 + LiCl + AlCl_3$$

$$SnCl_4 + LiAlH_4 \xrightarrow{\text{Ether}} SnH_4 + LiCl + AlCl_3$$

$$AlCl_3 + 3LiAlH_4 \longrightarrow 4AlH_3 + 3LiCl$$

(*v*) It reduces many organic compounds. For example, compounds containing carbonyl group (–CO) are reduced to alcohols.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2H \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

Uses. (*i*) It is extensively used in organic and inorganic chemistry as a versatile reducing agent.

(*ii*) It is used to prepare hydrides of elements like B, Al, Sn, etc.

SOLVED EXAMPLES

Example 1.

Would you expect the hydrides of N,O and F to have lower boiling points than the hydrides of their subsequent groups ? Explain. ***N.C.E.R.T.***

Solution:

The hydrides of N, O and F are NH_3, H_2O and HF respectively. On the basis of molecular masses of NH_3, H_2O and HF, their boiling points are expected to be lower than those of the subsequent group members (i.e., PH_3, H_2S, HCl). However, due to high electronegativity of N, O and F, their hydrides have strong intermolecular hydrogen bonding in their molecules.

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As a result of hydrogen bonding, the boiling points of NH_3, H_2O and HF are higher than the hydrides of their subsequent group members, which have almost negligible hydrogen bonding.

Example 2.

Comment upon the reactions of dihydrogen with

(i) Chlorine

(ii) Sodium and

(iii) Copper (II)oxide **N.C.E.R.T.**

Solution:

(*i*) Dihydrogen reduces chlorine to chloride (Cl^-) ion and itself gets oxidised to H^+ ion in HCl. An electron pair is shared between H and Cl to form a covalent molecule of hydrogen chloride.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl\ (g)$$

(*ii*) Sodium reduces dihydrogen to form hydride (H^-) ion and itself gets oxidised to sodium (Na^+) ion. During this reaction, an electron is transferred from Na to H leading to the formation of an ionic compound sodium hydride, Na^+H^-.

$$2Na(s) + H_2(g) \xrightarrow{\text{Heat}} 2Na^+H^-(s)$$

(*iii*) Hydrogen reduces copper (II) oxide to copper metal (in zero oxidation state) and itself gets oxidised to H_2O, which is a covalent molecule.

$$\overset{+1\ -2}{CuO} + \overset{0}{H_2}(g) \longrightarrow \overset{0}{Cu}(s) + \overset{+1\ -2}{H_2O}(l)$$

Example 3.

Can phosphorus with outer electronic configuration $3s^2 3p^3$ form PH_5 ? **N.C.E.R.T.**

Solution:

Though phosphorus exhibits +3 and +5 oxidation states, it cannot form PH_5. This is because of high enthalpy of atomisation ($\Delta_a H$) (435.89 kJ mol^{-1}) of dihydrogen and slightly negative electron gain enthalpy, $\Delta_{eg} H$ (–72.8 kJ mol^{-1}) of hydrogen, it acts only as a weak oxidising agent. Therefore, it can oxidise P to +3 oxidation state but not to its highest oxidation state of +5. Thus, P forms PH_3 but not PH_5.

WATER

Water is essential to all forms of life. It is most common, abundant and easily obtainable of all chemical compounds. It is a solvent of great importance and is regarded as a *universal solvent.* It is most studied of all chemical compounds. It can be easily transformed from liquid to solid and to gaseous states. It is the principal constituent of earth's surface. It is an important component of animal and vegetable matter and plays a vital role in their life processes. Water constitutes about 65% of our body and is an essential for its growth. We can live without food for some days but cannot live without water. Some plants have about 95% water.

Distribution of water over the earth's surface

Water is the principal constituent of earth's surface. The distribution of water over the earth's surface is not uniform. There is no permanent surface water in desert regions while the oceans cover vast areas of 78% of the earth surface *i.e.*, 1.61×10^8 km^2. They contain 97% of the available water. The fresh water amounts to only 2.7%, most of it is locked in Antarctic ice cap and in the Arctic. Antarctic ice cap covers 1.5×10^7 km^2 and contains $2.5 - 2.9 \times 10^7$ km^3 of fresh water.

Fresh water lakes contain 1.25×10^5 km^3 of water and more than half of which is in the four largest lakes :

Baikal (26,000 km^3), Tanganyika (20,000 km^3), Nayassa (13,000 km^3) and Superior (12,000 km^3). Fresh water is also present in many other smaller lakes, springs and rivers. The purification and recycling of water has now become major industry. The production of fresh water from sea and other saline water has been commercialised.

The estimated world water supply is

Source	Percentage of total
Oceans	97.33
Saline lakes and Inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

Apart from water, hydrogen and oxygen form another oxide namely **hydrogen peroxide** which has the molecular formula H_2O_2.

Structure of Water Molecule and its Aggregates

The molecule of water consists of two hydrogen atoms bonded to oxygen atom by covalent bonds. Oxygen atom (Z = 8, $1s^2\ 2s^2\ 2p^4$) has six electrons in its valence shell. Two of these valence electrons form bond pairs with two H atoms while the remaining four electrons remain as two lone pairs. Therefore, the oxygen atom in water is surrounded by four electron pairs and has tetrahedral geometry in which two positions are occupied by lone pairs as shown in Fig. 4 (*b*). Due to the presence of lone pairs, the geometry of water is distorted and the H—O—H bond angle is 104.5° which is less than the normal tetrahedral angle (109.5°). The geometry of the molecule is regarded as **angular** or **bent.** The O—H bond length in water is 95.7 pm.

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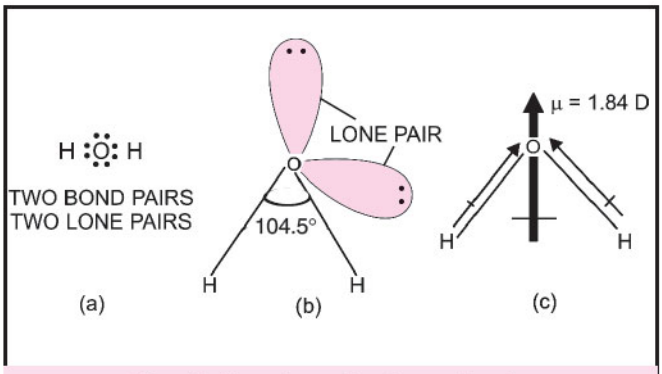

Fig. 4. Structure of water molecule.

Now, in water each O—H bond is polar because of the high electronegativity of oxygen (3.5) in comparison to that of hydrogen (2.1). The resultant dipole moment of water molecule is 1.84D.

Hydrogen Bonding in Water and Ice

Because of the polar nature of water molecule, the water molecules are held together by intermolecular hydrogen bonds in water. As a result, the water molecules are joined together in an extensive three dimensional network (Fig. 5). In this arrangement, each oxygen is tetrahedrally surrounded by four hydrogen atoms; two by covalent bonds and two by hydrogen bonds. Experimental studies have shown that liquid water and ice consists of aggregates of varying number of water molecules held together by hydrogen bonds. The resulting structure of ice is **open structure** having a number of vacant spaces. Therefore, *the density of ice is less*. When the ice melts, some of the hydrogen bonds are broken and the water molecules go in between the vacant spaces in the structure. As a result, the structure of liquid water is less open than structure of ice. Therefore, the density of water is more than that of ice. In other words, the density of ice is less than that of water and ***ice floats* over water**.

It may be noted that water has maximum density (1 g cm^{-3}) at 4°C (277 K). This property is very helpful for aquatic life. In severe cold, the upper layer of the sea water freezes. The heavier water (density more than that of ice) is present below the surface of ice. The ice layer formed on the surface of a lake in winter does not sink to the bottom. In fact, this provides a thermal insulation for the water below it. The sea animals can live safely in water under these conditions. Thus, it *ensures the survival of the aquatic life.*

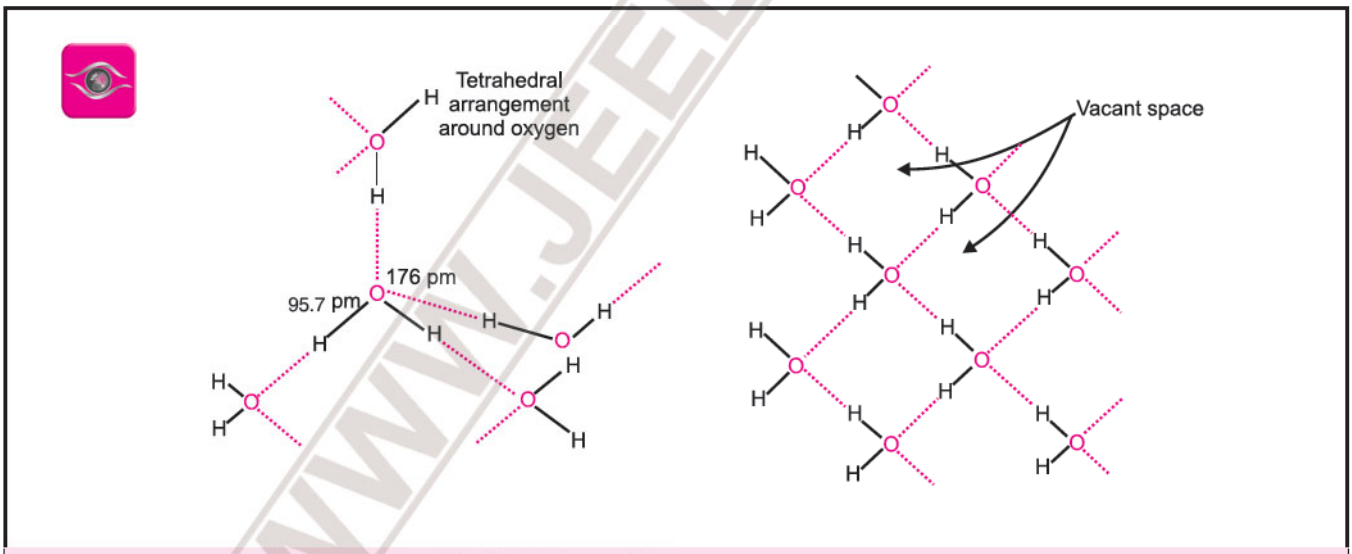

Fig. 5. Hydrogen bonding in water and ice.

Physical Properties of Water

Many of the properties of water are due to hydrogen bonding in their molecules. The important physical properties of water are :

(*i*) Water is liquid with freezing point of 273.2 K and boiling point of 373.2 K.

(*ii*) Water has maximum density of 1.00 g cm^{-3} at 277 K (4°C).

(*iii*) Water has strong hydrogen bonding in its molecules and exists as associated molecules, $(H_2O)_n$.

(*iv*) Water is polar in nature having dipole moment of 1.84D. It has solubility for a variety of substances and is regarded as a **universal solvent.**

Some of the important physical properties of water (H_2O) and heavy water (D_2O) containing isotope of hydrogen are listed in Table 6.

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Table 6. Some physical constants of H_2O and D_2O at 298 K.

Constant	Ordinary water (H_2O)	Heavy water (D_2O)
Molecular mass (g mol^{-1})	18.0151	20.0276
Maximum density (g cm^{-3}) at 298 K	1.0000	1.1059
Viscosity (centipoise)	0.8903	1.107
Melting point (K)	273.2	276.8
Boiling point (K)	373.2	374.4
Enthalpy of fusion (kJ mol^{-1}) at 273K	6.01	6.28
Enthalpy of vaporisation (kJ mol^{-1}) at 373K	40.66	41.61
Enthalpy of formation (kJ mol^{-1})	–285.9	–294.6
Ionisation constant	1.008×10^{-14}	1.95×10^{-15}
Dielectric constant	78.39	78.06
Electrical conductivity (293 K) (ohm^{-1} cm^{-1})	5.7×10^{-8}	—

Some of the **important observations** regarding the physical properties of water are :

(*i*) The freezing point, boiling point, heat of fusion and heat of vaporisation of water are higher as compared to the hydrides of the other members of same group (16) such as H_2S, H_2Se, H_2Te, etc. *This is due to the presence of hydrogen bonding in H_2O molecules which is absent in the hydrides of the rest of the members.*

(*ii*) Water has the capacity to dissolve most of the inorganic substances and is, therefore, regarded as a **universal solvent.** Most of the inorganic substances which are of ionic nature dissolve in water. Even few organic substances such as urea, alcohols, carbohydrates, etc. also dissolve in water. This is because of the presence of intermolecular hydrogen bonding in the molecules of the solute and water. Under very high pressure and temperature, water behaves as a non-polar solvent and dissolves organic compounds while common inorganic compounds are not dissolved.

When water freezes, it forms ice which is the crystalline form of water. Nine crystalline forms of ice are known. At atmospheric pressure, ice crystallises in the normal hexagonal form. However, at very low temperature, it condenses to cubic form. Many salts crystallise as hydrated salts from aqueous solutions. This type of association of water is essentially of five types such as **co-ordinated water, hydrogen bonded water, lattice water, zeolite water** and **clathrate water.**

Chemical Properties of Water

Water displays a versatile and unique chemical behaviour. It behaves as an *acid*, as a base, an *oxidant*, a *reductant* and as *ligand* to *metals*. Some of its characteristics are given below :

1. Stability of water. Water is quite stable and does not dissociate into its elements even at high temperatures. This is due to its high negative enthalpy of formation ($\Delta_f H = -285.9$kJ mol^{-1}). At about 1500 K, its decomposition to elements is only 2%.

$$2H_2O(g) \xrightarrow{1500K} 2H_2(g) + O_2(g)$$

However, when electricity is passed in the presence of a small amount of an acid or an alkali water decomposes to its elements.

$$2H_2O(l) \xrightarrow{\text{Electric current}} \underset{\text{(at cathode)}}{2H_2(g)} + \underset{\text{(at anode)}}{O_2(g)}$$

2. Acid-base character : Amphoteric nature of water. Water is a weak electrolyte and therefore, ionizes to a small extent to give $H_3O^+(aq)$ and $OH^-(aq)$ ions. Therefore, pure water has a small but measurable electrical conductivity and it dissociates as :

$$H_2O + H_2O \rightleftharpoons \underset{\text{Hydronium ion}}{H_3O^+} + OH^-$$

$K_w = 1.0 \times 10^{-14}$ mol^2 L^2 at 298K.

Water can act both as an acid and a base and is said to be *amphoteric*. According to Lowry Bronsted concept, it can act as an acid by losing a proton and as a base by accepting a proton. For example,

It behaves as a **base** towards hydrochloric acid or hydrogen sulphide (H_2S).

$$\underset{\text{(acid)}}{HCl\,(aq)} + \underset{\text{(Base)}}{H_2O\,(l)} \rightleftharpoons Cl^-\,(aq) + H_3O^+\,(aq)$$

$$\underset{\text{(acid)}}{H_2S\,(aq)} + \underset{\text{(Base)}}{H_2O\,(l)} \rightleftharpoons H_3O^+\,(aq) + HS^-(aq)$$

While it behaves as an **acid** towards ammonia,

$$\underset{\text{(Acid)}}{H_2O\,(l)} + \underset{\text{(Base)}}{NH_3\,(aq)} \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

In general, ***water can act as a base towards acids stronger than itself and as an acid towards bases stronger than it.*** The auto protolysis of water may be represented as :

$$\underset{Acid_1}{H_2O\,(l)} + \underset{Base_2}{H_2O\,(l)} \rightleftharpoons \underset{Acid_2}{H_3O^+\,(aq)} + \underset{Base_1}{OH^-\,(aq)}$$

It is therefore of great importance in acid base chemistry as discussed in Unit 7.

However, water is neutral towards litmus and its pH is 7.

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3. Oxidising and reducing nature. Water can act both as an oxidising and a reducing agent in its chemical reactions. Therefore, aqueous chemistry is very interesting for oxidation-reduction or redox reactions.

***(i)* As an oxidising agent :** Water can be reduced to H_2 by highly electropositive metals (having E° value $(M^{n+}|M)$ below – 0.83 V).

$$2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$$
$$E° = -0.83 \text{ V for } [OH^-] = 10^{-7} \text{ M}$$

Therefore, with active metals (highly electropositive) such as Na, Ca etc. (whose electrode potential is less than – 0.83 V), water can be easily reduced to dihydrogen :

$$\underset{\text{Oxidising agent}}{2Na(s) + H_2O(l)} \longrightarrow 2NaOH(aq) + H_2(g)$$

Thus, it is a great source of dihydrogen.

Similarly, when steam is passed over red hot coke (at 1273K), syn gas is formed.

$$C(s) + H_2O(g) \xrightarrow[Ni]{273\text{ K}} \underbrace{CO(g) + H_2(g)}_{\text{Syn gas}}$$

In this reaction also, water acts as an oxidising agent and itself gets reduced to dihydrogen.

***(ii)* As a reducing agent :** Water can also be oxidised according to the reaction :

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \quad E° = +1.23 \text{ V for } [H^+] = 10^{-7} \text{ M}$$

Therefore, water reacts with highly electronegative elements behaving as reducing agent. For example, with fluorine, water acts as a reducing agent and hence itself gets oxidised to O_2 or O_3.

$$\underset{\text{Reducing agent}}{2F_2(g) + 2H_2O(l)} \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$\text{or } 3F_2(g) + 3H_2O(l) \longrightarrow O_3(g) + 6H^+(aq) + 6F^-(aq)$$

Water reacts with chlorine and bromine similar to reaction with fluorine.

Another typical example of this type of reaction are oxidation of H_2O to O_2 during photosynthesis.

$$6CO_2(g) + 12H_2O(l) \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$$

4. Hydrolysis reactions. Water has very strong solvating power due to its high dielectric constant. Therefore, it acts as an excellent solvent. Because of great affinity of many elements for oxygen, water can easily hydrolyse many ionic and covalent compounds of non-metals. For example,

(*i*) Water hydrolyses oxides and halides of non-metals forming their respective acids.

$$CaO(s) + H_2O(l) \longrightarrow \underset{\text{Calcium hydroxide}}{Ca(OH_2)(aq)}$$

$$SO_2(g) + H_2O(l) \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_3(aq)}$$

$$\underset{\text{Phosphorus pentoxide}}{P_4O_{10}(s)} + 6H_2O(l) \longrightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4(aq)}$$

$$SO_3(g) + H_2O(l) \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_4(aq)}$$

$$PBr_3(l) + 3H_2O(l) \longrightarrow \underset{\text{Phosphorous acid}}{H_3PO_3(aq)} + 3HBr(aq)$$

$$SiCl_4(l) + 2H_2O(l) \longrightarrow \underset{\text{Hydrochloric acid}}{SiO_2(s)} + 4HCl(aq)$$

$$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$$

(*ii*) Water hydrolyses the carbides, hydrides, nitrides and phosphides of some metals.

$$\underset{\text{Cal. carbide}}{CaC_2} + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

$$\underset{\substack{\text{Aluminium}\\\text{carbide}}}{Al_4C_3} + 12H_2O \longrightarrow 4Al(OH)_3 + \underset{\text{Methane}}{3CH_4}$$

$$\underset{\text{Cal. hydride}}{CaH_2(s)} + 2H_2O(l) \longrightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2(aq)} + 2H_2(g)$$

$$\underset{\text{Cal. phosphide}}{Ca_3P_2} + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{\text{Phosphine}}{2PH_3}$$

$$\underset{\text{Calcium nitride}}{Ca_3N_2(s)} + 6H_2O(l) \longrightarrow 3Ca(OH)_2 + \underset{\text{Ammonia}}{2NH_3}$$

$$\underset{\text{Magnesium nitride}}{Mg_3N_2} + 6H_2O \longrightarrow 3Mg(OH)_2 + \underset{\text{Ammonia}}{2NH_3}$$

$$\underset{\text{Aluminium nitride}}{AlN} + 3H_2O \longrightarrow Al(OH)_3 + \underset{\text{Ammonia}}{NH_3}$$

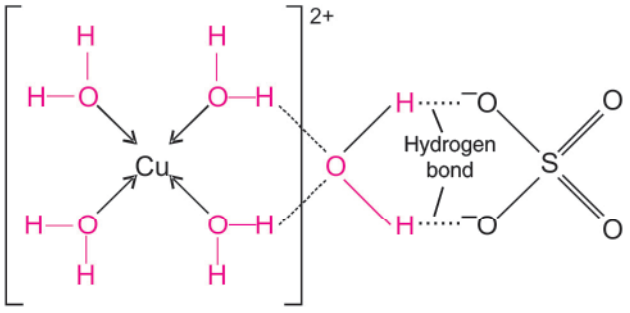
5. Hydration reactions. Water has strong ability to form compounds with some metal salts known as **hydrates.** These hydrates can be classified into three types :

(*i*) *Water molecules are co-ordinated to metal ion in a complex.*

$$Ni^{2+} + 6H_2O \longrightarrow [Ni(H_2O)_6]^{2+}$$

Some other examples are $[Cr(H_2O)_6]Cl_3$, $[Fe(H_2O)_6]Cl_3$, etc.

(*ii*) *Water molecules may be hydrogen bonded to certain oxygen containing anions.* For example, in $CuSO_4 . 5H_2O$, four H_2O molecules are co-ordinated to Cu^{2+} ion while the fifth H_2O molecule is hydrogen bonded to SO_4^{2-} ion.



(*iii*) *Water molecules may occupy the interstitial sites (voids) in the crystal lattice.* For example, $BaCl_2 . 2H_2O$.

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HEAVY WATER

Chemically heavy water is deuterium oxide (D_2O). It was discovered by *Urey* in 1932. He showed that ordinary water contains small proportion (about 1 part in 5000) of D_2O. It can be prepared by **the prolonged electrolysis of water or by fractional distillation.** When water is electrolysed, H_2 is liberated much faster than D_2 and the remaining water becomes enriched in heavy water, D_2O. If the process is continued until only a small volume remains, then almost pure D_2O is obtained. It has been estimated that about 29,000 L of water must be electrolysed to get 1L of D_2O that is 99% pure.

PHYSICAL PROPERTIES

Like ordinary water, it is colourless, odourless and tasteless liquid. The physical constants of heavy water are generally slightly higher than ordinary water (H_2O). This is quite expected because the molecular mass of heavy water is more than ordinary water. The dielectric constant of D_2O is slightly lower than that of H_2O and therefore, ionic compounds are less soluble in D_2O than in H_2O. Some of the important physical constants of heavy water are compared with water in Table 6.

CHEMICAL PROPERTIES

Heavy water differs only slightly from ordinary water in its chemical properties. However, *the reactions of D_2O are slightly slower than those of H_2O.* Some of the important chemical reactions of heavy water are discussed below :

1. Action with metals. D_2O reacts with alkali and alkaline earth metals slowly liberating deuterium.

$$2Na + 2D_2O \longrightarrow \underset{\text{Sodium deuteroxide}}{2NaOD} + D_2$$

$$Ca + D_2O \longrightarrow \underset{\text{Calcium deuteroxide}}{Ca(OD)_2} + D_2$$

2. Action with metallic oxides. Basic oxides of metals like Na, Ca, etc. dissolve in D_2O forming heavy alkalies.

$$Na_2O + D_2O \longrightarrow \underset{\text{Sodium deuteroxide}}{2NaOD}$$

$$CaO + D_2O \longrightarrow \underset{\text{Calcium deuteroxide}}{Ca(OD)_2}$$

3. Action with non–metallic oxides. Non-metallic oxides such as phosphorus pentoxide (P_2O_5), sulphur trioxide (SO_3) etc. readily dissolve in heavy water forming their corresponding deuteroacids.

$$P_2O_5 + 3D_2O \longrightarrow \underset{\text{Deutero phosphoric acid}}{2D_3PO_4}$$

$$SO_3 + D_2O \longrightarrow \underset{\text{Deutero sulphuric acid}}{D_2SO_4}$$

4. Action with carbides, nitrides, phosphides, arsenides, etc. The reactions of D_2O with these compounds are similar to those of water. For example :

$$\underset{\text{Calcium carbide}}{CaC_2} + 2D_2O \longrightarrow Ca(OD)_2 + \underset{\text{Deutero acetylene}}{C_2D_2}$$

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 2D_2O \longrightarrow 4Al(OD)_3 + \underset{\text{Deutero methane}}{3CD_4}$$

$$\underset{\text{Magnesium nitride}}{Mg_3N_2} + 6D_2O \longrightarrow 3Mg(OD)_2 + \underset{\text{Deutero ammonia}}{2ND_3}$$

$$\underset{\text{Calcium phosphide}}{Ca_3P_2} + 6D_2O \longrightarrow 3Ca(OD)_2 + \underset{\text{Deutero phosphine}}{2PD_3}$$

$$\underset{\text{Sodium arsenide}}{Na_3As} + 3D_2O \longrightarrow 3NaOD + \underset{\text{Deutero arsine}}{AsD_3}$$

5. Electrolysis. On electrolysis, heavy water decomposes to give deuterium and oxygen, which are liberated at cathode and anode respectively.

$$2D_2O \longrightarrow \underset{\text{Deuterium}}{2D_2} + O_2$$

6. Exchange reactions. When compounds containing hydrogen are treated with D_2O, hydrogen undergoes exchange for deuterium.

$$NaOH + D_2O \longrightarrow NaOD + HOD$$

$$NH_4Cl + 4D_2O \longrightarrow ND_4Cl + 4HOD$$

$$HCl + D_2O \rightleftharpoons \underset{\text{Deutero chloride}}{DCl} + HOD$$

$$\underset{\text{Chloroform}}{CHCl_3} + D_2O \rightleftharpoons \underset{\text{Deutero chloroform}}{CDCl_3} + HOD$$

7. Formation of deuterates. Like ordinary water, heavy water combines with many compounds as heavy water of crystallization. These heavy water hydrates are also called **deuterates**. For example,

$CuSO_4.5D_2O$, $MgSO_4.7D_2O$, $NiCl_2.6D_2O$, $CoCl_2.6D_2O$, $Na_2SO_4.10D_2O$, etc.

8. Biological properties. Heavy water is injurious to plants, animals and human beings because it slows down the rates of reactions occurring in them.

Thus, ***heavy water does not support life so well as does ordinary water***.

Uses of heavy water :

1. **As a moderator**. Heavy water has been finding use in *nuclear reactors* as a ***moderator*** because it slows down the fast moving neutrons and therefore, helps in controlling the nuclear fission process.
2. **As a tracer compound**. Heavy water has also been used as a tracer compound to study mechanism of many chemical reactions.
3. **In nuclear magnetic resonance**. Heavy water is used as one of the reference in nuclear magnetic resonance spectroscopy.

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4. **For the preparation of deuterium**. Heavy hydrogen or deuterium can be obtained by the electrolysis of heavy water or by its decomposition by sodium metal.

HARD AND SOFT WATER

Natural water contains dissolved salts. Depending upon its behaviour towards soap solution, water may be classified as *soft water* or *hard water*.

(a) Soft water. *Water which produces lather with soap solution readily is called* **soft water.** For example, distilled water, rain water and demineralised water.

(b) Hard water. *Water which does not produce lather with soap solution readily is called* **hard water.** For example, sea water, river water, well water and tap water.

Cause of Hardness of Water

The hardness of water *is due to the presence of the bicarbonates, chlorides and sulphates of calcium and magnesium*. These salts dissolve in water when it passes through the grounds or rocks. Hard water does not produce **lather** because the cations (Ca^{2+} and Mg^{2+}) present in hard water react with soap to form insoluble precipitates. Soaps are sodium salts of higher fatty acids like stearic acid ($C_{17}H_{35}COOH$), oleic acid ($C_{17}H_{33}COOH$) or palmitic acid ($C_{17}H_{31}COOH$). When soap is added to hard water, these anions combine with Ca^{2+} and Mg^{2+} ions to form calcium and magnesium salts which are insoluble in water.

$$\underset{\text{From hard water}}{M^{2+}} + 2\underset{\text{Sodium stearate (soap)}}{C_{17}H_{35}COONa} \longrightarrow \underset{\text{Metal stearate (precipitate)}}{(C_{17}H_{35}COO)_2M}\downarrow + 2Na^+$$

where M = Ca or Mg

Therefore, no lather is produced until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap.

Therefore, hard water is unsuitable for laundry washing and dyeing. In addition hard water is also harmful for steam boilers. The inner surface of the boiler gets crusted with scale known as *boiler scale*. It is mainly calcium sulphate, calcium carbonate and magnesium oxychloride. The deposition of scale decreases the efficiency of the boiler and also damages it. Therefore, hard water should not be used in boilers.

Type of Hardness of Water

The hardness of water is of two types : *temporary hardness* and *permanent hardness*.

(a) Temporary hardness. This type of hardness in water is due to the presence of *bicarbonates of calcium and magnesium dissolved in it*. The hardness is called temporary because it can be very easily removed by simply boiling the hard water for some time. Temporary hardness is also called **carbonate hardness.**

(b) Permanent hardness. *This hardness is due to the presence of chlorides and sulphates of calcium and magnesium dissolved in water*. Since the hardness cannot be easily removed, it is therefore, called permanent hardness. The permanent hardness is also called **non-carbonate hardness.**

Softening of Water

The process of the removal of hardness from water is called **softening of water.**

I. Removal of temporary hardness. Temporary hardness of water is due to the presence of bicarbonates of calcium and magnesium. It can be removed by the following methods :

1. By boiling. The temporary hardness of water can be removed by *boiling the hard water in large boilers*. During boiling, the bicarbonates of calcium and magnesium decompose into insoluble carbonates and give CO_2. The insoluble carbonates can be removed by filtration.

$$\underset{\text{Cal. bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{ppt}}{CaCO_3}\downarrow + CO_2\uparrow + H_2O$$

$$\underset{\text{Mag. bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{ppt}}{MgCO_3}\downarrow + CO_2\uparrow + H_2O$$

2. Calcium hydroxide method (Clark's method). This process is used on a commercial scale. In this process, calculated amount of lime (calcium hydroxide) is added to temporary hard water. The soluble bicarbonates present in water are converted into insoluble carbonates which settle at the bottom of the tank and are removed by filtration.

$$\underset{\text{(Soluble)}}{Ca(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH)_2} \longrightarrow \underset{\text{(Insoluble)}}{2CaCO_3}\downarrow + 2H_2O$$

$$\underset{\text{(Soluble)}}{Mg(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH)_2} \longrightarrow \underset{\text{(Insoluble)}}{MgCO_3}\downarrow + CaCO_3\downarrow + 2H_2O$$

In this method, *excess of lime should not be added, otherwise water will again become hard due to absorption of CO_2 from the atmosphere by reacting with unused excess calcium hydroxide. Calcium bicarbonate formed will make water hard.*

$$Ca(OH)_2 + 2CO_2 \longrightarrow Ca(HCO_3)_2$$

II. Removal of permanent hardness. Permanent hardness cannot be removed by boiling. It can be removed by the following methods :

1. By washing soda method. In this method, water is treated with a calculated amount of washing soda (Na_2CO_3) which converts the chlorides and sulphates of calcium and magnesium into their respective carbonates which get precipitated.

$$CaCl_2 + Na_2CO_3 \longrightarrow \underset{\text{ppt}}{CaCO_3}\downarrow + 2NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow \underset{\text{ppt}}{MgCO_3}\downarrow + Na_2SO_4$$

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Thus, water becomes free from the Ca^{2+} and Mg^{2+} ions and becomes soft.

2. Ion exchange method. This is a modern method employed for the softening of hard water. In this method, the ions responsible for the hardness of water are exchanged by certain less damaging ions present in some chemical compounds called **ion-exchangers**. These exchangers are of two types :

(A) Inorganic cation exchangers (*Permutit or zeolite method*). These are complex inorganic salts like hydrated sodium aluminium silicate, $Na_2Al_2Si_2O_8 . x\,H_2O$ which have interesting property of exchanging cations such as calcium and magnesium ions in hard water with sodium ions. These complex salts are known as **zeolites**. These can be either naturally occurring or artificially synthesised substances. Their technical name is **permutit.** For artificial synthesis of permutit, a mixture of soda ash (Na_2CO_3), sand (SiO_2) and alumina (Al_2O_3) is fused. The product is washed with water to remove soluble impurities leaving behind a porous mass of permutit.

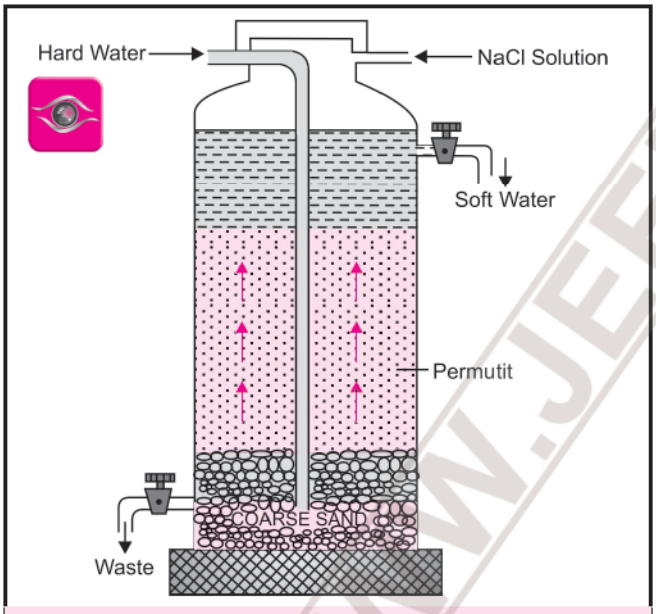

Fig. 6. Permutit method for softening of hard water.

The permutit is loosely packed in a big tank over a layer of coarse sand (Fig. 6). Hard water is introduced into the tank from the top. Water reaches the bottom of the tank and then slowly rises through the permutit layer in the tank. The cations present in hard water are exchanged for sodium ions.

$$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{\text{(from hard water)}}{Ca^{2+}} \longrightarrow \underset{\text{Calcium zeolite}}{CaZ} + 2Na^+$$

$$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{\text{(from hard water)}}{Mg^{2+}} \longrightarrow \underset{\text{Magnesium zeolite}}{MgZ} + 2Na^+$$

where $Z = Al_2Si_2O_8 . x\,H_2O$

The calcium and magnesium ions remain attached to the zeolite and the water becomes soft. The soft water contains sodium salts (which are soluble in water). These sodium salts do not precipitate the soap and do not interfere with lather formation.

Regeneration of Permutit. As the process continues, the zeolite gets exhausted because the whole of sodium zeolite gets converted to calcium or magnesium zeolite. It may be regenerated by passing 10% solution of sodium chloride through it. The following reactions take place :

$$\underset{\text{(exhausted zeolite)}}{CaZ} + 2Na^+ \longrightarrow \underset{\text{(regenerated zeolite)}}{Na_2Z} + Ca^{2+}$$

$$\underset{\text{(exhausted zeolite)}}{MgZ} + 2Na^+ \longrightarrow \underset{\text{(regenerated zeolite)}}{Na_2Z} + Mg^{2+}$$

The regenerated sodium zeolite can be used again for the softening of water.

(B) Synthetic resins or organic ion exchangers (*ion exchange resins*). These are insoluble polymeric solids having giant hydrocarbon network containing reactive acidic or basic groups. These are manufactured in bead form and are permeable to water. These are called **ion exchange resins**. These are superior to zeolites because they can remove all types of cations as well as anions present in water. The resulting water is known as **demineralised** or **deionised water.**

These are essentially of two types :

(*i*) **Cation exchange resins.** These contain giant hydrocarbon framework attached to acidic groups such as —COOH (carboxyl) or $—SO_3H$ (sulphonic acid). These are capable of exchanging the H^+ with the cations of the hard water and are called **cation exchange resins** or **cation exchangers.** These may be represented as resin $—H^+$.

(*ii*) **Anion exchange resins.** These resins contain giant hydrocarbon framework attached to basic groups such as $—OH^-$ (hydroxide) or $—NH_2$ (amine) group. These groups are usually present in the form of substituted ammonium hydroxides as

$$\text{Resin} - NH_2(s) + H_2O(l) \longrightarrow \text{Resin} - NH_3^+OH^-(s)$$

Therefore, these may be represented as resin $—NH_3^+OH^-$ or simply as Resin $—OH^-$. These resins are capable of exchanging the OH^- ions with the anions of hard water and are called **anion exchange resins** or simply as **anion exchangers.**

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Method of removal of hardness by organic exchanger

The hard water is first passed through a bed of cation exchange resin (Fig. 7). All the cations present in hard water will exchange with H^+ ions of the resin as :

$$2Resin - H^+ + 2M^+(aq) \longrightarrow M(Resin)_2 + 2H^+$$
(Exhausted resin)

$(M = Ca^{2+}, Mg^{2+})$

e.g., $2Resin - H^+ + Ca^{2+} + 2Cl^- \longrightarrow$
(in hard water) $Ca(Resin)_2 + 2H^+ + 2Cl^-$
(Exhausted resin)

$2Resin - H^+ + Mg^{2+} + SO_4^{2-} \longrightarrow$
(in hard water) $Mg(Resin)_2 + 2H^+ + SO_4^{2-}$
(Exhausted resin)

Therefore, water which comes out from the bottom of the first tank will be richer in H^+ ions. This water is then passed through a bed of anion exchange resin which exchanges its OH^- with Cl^- ions and SO_4^{2-} ions present in hard water as :

$$Resin - NH_3^+ OH^- + Cl^- \longrightarrow Resin\ NH_3^+Cl^- + OH^-$$
in hard water Exhausted resin

$$2Resin - NH_3^+ OH^- + SO_4^{2-} \longrightarrow (Resin\text{–}NH_3^+)_2\ SO_4^{2-} + 2OH^-$$

Thereafter, the H^+ ions (formed in the first tank) combine with the OH^- ions (formed in the second tank) to produce water.

$$H^+ + OH^- \longrightarrow H_2O$$

Thus, water obtained by this method is free from all types of cations as well as anions and is called **deionised water.**

Regeneration of resins. The exhausted resin in the first tank is regenerated by treatment with moderately concentrated hydrochloric or sulphuric acid.

$$(Resin)_2Ca + 2HCl \longrightarrow CaCl_2 + 2\ Resin\text{—}H^+$$
(exhausted resin) (regenerated resin)

The exhausted resin in the second tank is regenerated by treatment with moderately concentrated solution of sodium hydroxide.

$$Resin\text{–}NH_3^+Cl^- + NaOH \longrightarrow$$
Exhausted resin $Resin\text{–}NH_3^+OH^- + Na^+ + Cl^-$
Regenerated resin

3. By Calgon's process (*Sequestration*). This is the most modern method of the softening of water. In this method, the harmful Ca^{2+} and Mg^{2+} ions present in hard water are sequestered (rendered ineffective) in the form of soluble complexes by adding some substances. For example, hard water is treated with sodium polymetaphosphate $(NaPO_3)_n$ (where n is as high as 1000), commercially known as **calgon** (meaning calcium gone). The commonly used calgon is sodium hexametaphosphate, $Na_6P_6O_{18}$ or $Na_2[Na_4(PO_3)_6]$. Calgon combines with calcium and magnesium ions to form complex ions which are soluble in water as :

$$Na_2[Na_4(PO_3)_6] + 2Ca^{2+} \longrightarrow Na_2[Ca_2(PO_3)_6] + 4Na^+$$
Calgon Complex salt (soluble)

$$Na_2[Na_4(PO_3)_6] + 2Mg^{2+} \longrightarrow Na_2[Mg_2(PO_3)_6] + 4Na^+$$
Calgon Complex salt (soluble)

The complexed calcium and magnesium ions do not form any precipitate with soap. Therefore, water can easily form lather with soap.

HYDROGEN PEROXIDE

Hydrogen peroxide was discovered by a French chemist **J. L. Thenard** in 1818. Its molecular formula is H_2O_2.

Preparation of hydrogen peroxide.

1. Hydrogen peroxide can be prepared in the **laboratory** by the action of cold, dilute sulphuric acid on sodium or barium peroxide.

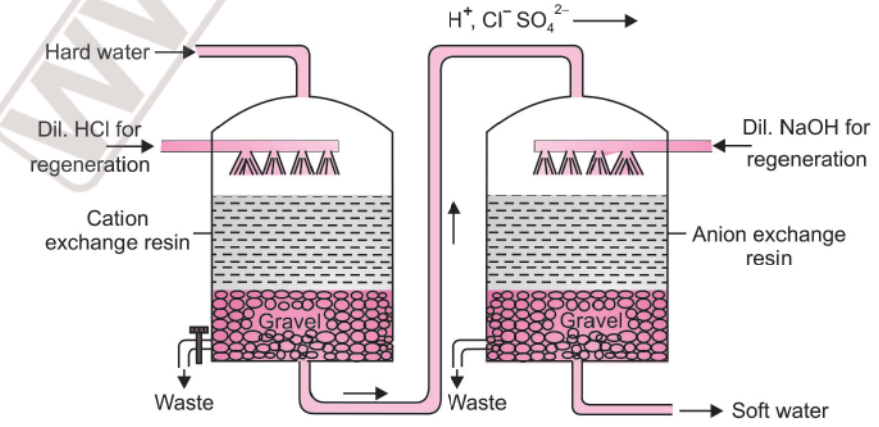

Fig. 7. Removal of hardness by the organic ion exchanger.

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(a) From sodium peroxide (Merck's process). Hydrogen peroxide is prepared by adding calculated amounts of sodium peroxide to ice cold dilute (20%) solution of sulphuric acid. The addition is carried out slowly in small amounts with constant stirring.

$$\underset{\text{Sodium peroxide}}{Na_2O_2} + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

Upon cooling, crystals of $Na_2SO_4.10H_2O$ separate out. The crystals of $Na_2SO_4.10H_2O$ are decanted leaving behind solution of hydrogen peroxide. In this method, 30% hydrogen peroxide is obtained.

(b) From barium peroxide. Hydrogen peroxide was first prepared by J.L. Thenard in 1818 by acidifying barium peroxide and removal of excess water by evaporation under reduced pressure. In this method, a paste of hydrated barium peroxide is prepared in ice cold water and is treated with about 20% ice cold solution of sulphuric acid.

$$\underset{\text{Hydrated barium peroxide}}{BaO_2.8H_2O(s)} + H_2SO_4(aq) \longrightarrow \underset{\text{(ppt)}}{BaSO_4(s)} + H_2O_2(aq) + 8H_2O(l)$$

The white precipitate of barium sulphate is removed by filtration leaving behind about 5% solution of hydrogen peroxide. In this method, *anhydrous barium peroxide is not used because barium sulphate forms a protective layer around unreacted barium peroxide which prevents its further participation in the chemical reaction.*

Limitation of the method. The hydrogen peroxide solution prepared by this method contains some heavy Ba^{2+} ions. These catalyse the decomposition of hydrogen peroxide and, thus, the solution cannot be stored for a long time. To prevent this, sulphuric acid is replaced by phosphoric acid. In this method, barium phosphate gets completely precipitated and the solution does not contain any free Ba^{2+} ions to catalyse the decomposition of hydrogen peroxide.

$$3BaO_2.8H_2O + 2H_3PO_4 \longrightarrow \underset{\text{(ppt)}}{Ba_3(PO_4)_2} + 24H_2O + 3H_2O_2$$

Manufacture of Hydrogen Peroxide

On a commercial scale, hydrogen peroxide can be prepared by the following methods :

(a) By electrolysis of 50% H_2SO_4 solution. In this method, a 50% solution of sulphuric acid is electrolysed at high current density in an electrolytic cell when peroxodisulphuric acid is formed at the anode.

$$2H_2SO_4 \xrightarrow{\text{Electrolysis}} \underset{\text{Peroxodisulphuric acid}}{HO_3SOOSO_3H\ (aq)\ \text{or}\ H_2S_2O_8\ (aq)} + H_2(g)$$

The electrolysis occurs as :

$$H_2SO_4 \longrightarrow \underset{\text{Anode}}{HSO_4^-} + \underset{\text{Cathode}}{H^+}$$

At cathode

$$2H^+ + 2e^- \longrightarrow 2H \text{ or } H_2$$

At anode

$$2HSO_4^- \longrightarrow \underset{\text{Peroxodisulphuric acid}}{H_2S_2O_8} + 2e^-$$

Peroxodisulphuric acid (formed around anode) is drawn off from the cell and hydrolysed with water to give hydrogen peroxide.

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

The resulting solution is distilled under reduced pressure when hydrogen peroxide gets distilled while sulphuric acid with high boiling point, remains undistilled.

Recent modification. The above method has been modified by using equimolar mixture of sulphuric acid and ammonium sulphate for electrolysis.

$$\underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4} + \underset{\text{Sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{Ammonium hydrogen sulphate}}{2NH_4HSO_4}$$

$$2NH_4HSO_4 \rightleftharpoons \underset{\text{Anode}}{2NH_4SO_4^-} + \underset{\text{Cathode}}{2H^+}$$

At cathode

$$2H^+ + 2e^- \longrightarrow 2H \text{ or } H_2$$

At anode

$$2NH_4SO_4^- \longrightarrow \underset{\text{Ammonium persulphate}}{(NH_4)_2\,S_2O_8} + 2e^-$$

Ammonium persulphate is withdrawn and distilled with water to get hydrogen peroxide

$$(NH_4)_2\,S_2O_8 + 2H_2O \longrightarrow 2\,NH_4HSO_4 + H_2O_2$$

This method is now being used for the laboratory preparation of D_2O_2.

$$K_2S_2O_8(s) + 2D_2O(l) \longrightarrow 2\,KDSO_4(aq) + D_2O_2(l)$$

(b) From 2-Ethyl anthraquinol. On an industrial scale, hydrogen peroxide can be obtained by the auto-oxidation of an organic compound, 2-ethyl anthraquinol.

$$\text{2-Ethyl anthraquinol} \underset{H_2/Pd}{\overset{O_2\ (air)}{\rightleftharpoons}} \text{Oxidised product} + H_2O_2.$$

The method involves the following steps :

(*i*) 2-Ethyl anthraquinone is dissolved in benzene and hydrogen gas is passed through the solution in

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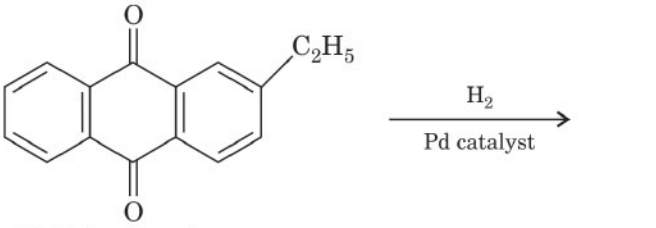
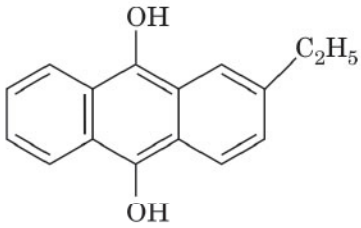
the presence of paladium (Pd) catalyst when the compound is reduced to 2-ethyl anthraquinol.

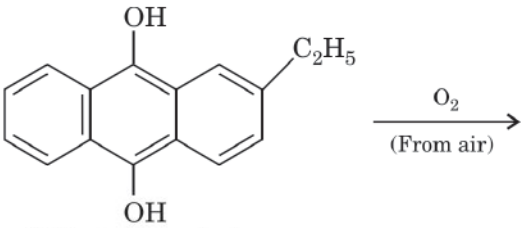


2-Ethyl anthraquinone

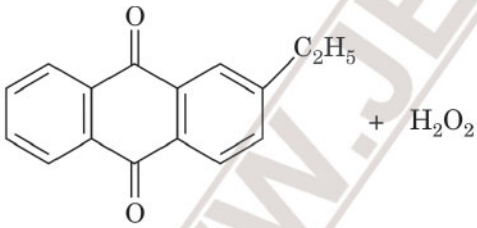


2-Ethyl anthraquinol

(*ii*) The reduced product is dissolved in a mixture of benzene and cyclohexanol and upon passing air, it is oxidised back to 2-ethyl anthraquinone and hydrogen peroxide is produced.



2-Ethyl anthraquinol



2-Ethyl anthraquinone

The 2-ethyl anthraquinone formed can be used again in the first step. In short, in this process only dihydrogen and atmospheric oxygen are used up to form hydrogen peroxide and 2-ethyl anthraquinone is not used up.

The net reaction is

$$H_2 + O_2 \longrightarrow H_2O_2$$

This process is, therefore, very cheap and is widely used for the manufacture of hydrogen peroxide.

Concentration of Hydrogen Peroxide

The hydrogen peroxide obtained (about 1%) by the above methods is extracted with water and the aqueous solution is concentrated. It may be noted that the concentration of the solution cannot be done by simple boiling because, hydrogen peroxide decomposes below its boiling point.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Further the decomposition of H_2O_2 is catalysed by presence of heavy metal ion impurities, dust and rough and uneven surfaces. The concentration may be done by the following steps :

(*i*) **Evaporation on a water bath.** The dilute solution of hydrogen peroxide is transferred to an evaporating dish and warmed carefully on a water bath. In this process about 30% solution of H_2O_2 is obtained.

(*ii*) **Dehydration in a vacuum desiccator.** The above solution of hydrogen peroxide is placed over concentrated sulphuric acid in a *vacuum desiccator* (Fig. 8). The water vapours are absorbed by concentrated sulphuric acid and, thus, about 90% concentrated solution of hydrogen peroxide is obtained.

(*iii*) **Distillation under reduced pressure.** The 90% solution of hydrogen peroxide is then distilled under reduced pressure (10–15 mm). During this process, water distils over at 303–313 K and 99% pure hydrogen peroxide is left behind.

(*iv*) **Removal of last traces of water.** The 99% solution of hydrogen peroxide is cooled in a freezing mixture of solid carbon dioxide and ether. As a result of this, crystals of hydrogen peroxide separate out which are removed, dried and remelted. This gives completely pure hydrogen peroxide.

Storage of hydrogen peroxide. The following precautions must be taken while storing hydrogen peroxide :

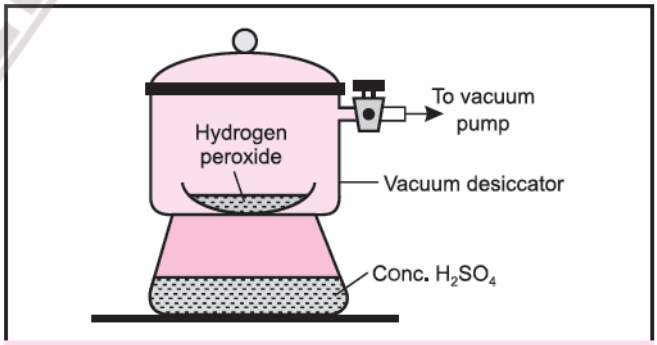


Fig. 8. Vacuum desiccator.

(*a*) It must be kept in wax lined coloured bottles because the rough glass surface causes its decomposition.

(*b*) A small amount of *phosphoric acid, glycerol* or *acetanilide* is generally added which retard the decomposition of H_2O_2. These are also called **negative catalysts**.

Properties of Hydrogen Peroxide

Physical Properties

(*i*) Pure hydrogen peroxide is a thick syrupy liquid with pale blue colour.

(*ii*) It is more viscous, less volatile and dense than water.

(*iii*) Its density is 1.44 g cm^{-3}.

(*iv*) Its melting point is 272.4 K and boiling point is 358 K at 68 mm of Hg pressure.

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(*v*) It is completely miscible with water, alcohol and ether in all proportions. It forms a hydrate with water as $H_2O_2.H_2O$ (m.p. 221 K).

The important physical characteristics of H_2O_2 are given in Table 7.

Table 7. Physical characteristics of H_2O_2

Physical property	Value
Melting point (K)	272.4
Boiling point (K)	423
Vapour pressure (at 298 mm Hg)	1.9
Density (solid at 268.5 K) 1 g cm^{-3}	1.6434
Density (liquid at 298 K) 1 g cm^{-3}	1.4425
Viscosity (290 K) cP.	1.245
Dielectric constant (288 K)	70.7
Electrical conductivity (at 298 K) ohm^{-1} cm^{-1}	5.1×10^{-8}

Chemical Properties

1. Decomposition. Pure hydrogen peroxide is an unstable liquid and decomposes into water and oxygen either upon standing or upon heating.

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)\,;\quad \Delta H = -196.0 \text{ kJ}$$

In H_2O_2, the oxidation state of oxygen is –1 which is intermediate between the values for O_2 (zero) and H_2O (–2). Therefore, aqueous solution of H_2O_2 readily disproportionates (decomposes).

The decomposition is further accelerated by the presence of metals like platinum, gold, metal oxides (MnO_2) or by certain metal ions such as Fe^{2+} ions. Even rough surface favours its decomposition.

It is also decomposed by exposure to light. It is therefore, stored in wax-lined glass or plastic vessels in the presence of stabilizers like urea. It is kept away from dust because dust (even in small quantities) induces explosive decomposition.

2. Acidic nature. Pure hydrogen peroxide is a weak acid ($K_a = 1.55 \times 10^{-12}$ at 298 K) and dissociates as :

$$H_2O_2 + H_2O \longrightarrow H_3O^+ + \underset{\text{Hydroperoxide ion}}{HO_2^-}$$

$$HO_2^- + H_2O \longrightarrow H_3O^+ + \underset{\text{Peroxide ion}}{O_2^{2-}}$$

It forms two types of salts. For example,

$$NaOH + H_2O_2 \longrightarrow \underset{\text{Sod. hydroperoxide (Acidic salt)}}{NaHO_2} + H_2O$$

$$2NaOH + H_2O_2 \longrightarrow \underset{\text{Sod. peroxide (Normal salt)}}{Na_2O_2} + 2H_2O$$

3. Oxidising and reducing character. Hydrogen peroxide behaves as an oxidising agent as well as reducing agent in both acid and alkaline solution. The oxidation state of oxygen in hydrogen peroxide is –1. It can, therefore, be oxidised to O_2 (zero oxidation state) or reduced to H_2O or OH^- (–2 oxidation state for oxygen). However, ***it is a powerful oxidising agent but a weak reducing agent***. For example,

Oxidising character.

Hydrogen peroxide acts as an oxidising agent both in **acidic** as in **alkaline** solutions as :

In acidic medium

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$

In basic medium

$$H_2O_2 + OH^- + 2e^- \longrightarrow 3OH^-$$

or

$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$

Some important reactions in which H_2O_2 acts as an oxidising agent are given below :

***(a)* Oxidising action in acidic medium.**

In the presence of an acid, H_2O_2 can accept electrons and, thus acts as an oxidising agent.

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$

(*i*) *H_2O_2 oxidises ferrous sulphate to ferric sulphate*

$$H_2O_2 \longrightarrow H_2O + O$$
$$2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O$$
$$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$

or $2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$

(*ii*) *H_2O_2 oxidises acidified potassium ferrocyanide to potassium ferricyanide*

$$H_2O_2 \longrightarrow H_2O + O$$
$$2K_4[Fe(CN)_6] + H_2SO_4 + O \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + H_2O$$
$$2K_4[Fe(CN)_6] + H_2SO_4 + H_2O_2 \longrightarrow \underset{\text{Pot. ferrocyanide}}{2K_3[Fe(CN)_6]} + K_2SO_4 + 2H_2O$$

or $2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^+ \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$

(*iii*) *H_2O_2 liberates iodine from acidified potassium iodide solution.*

$$H_2O_2 \longrightarrow H_2O + O$$
$$2KI + H_2SO_4 + O \longrightarrow K_2SO_4 + I_2 + H_2O$$
$$2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + I_2 + 2H_2O$$

or $2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$

(*iv*) *H_2O_2 oxidises ice cold acidified potassium dichromate solution (containing some ether) to chromium pentoxide.*

$$H_2O_2 \longrightarrow H_2O + O\ ] \times 4$$
$$K_2Cr_2O_7 + H_2SO_4 + 4[O] \longrightarrow K_2SO_4 + 2CrO_5 + H_2O$$
$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow K_2SO_4 + \underset{\text{Chromium pentoxide}}{2CrO_5} + 5H_2O$$

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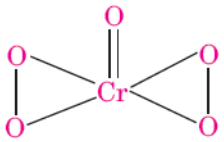
Chromium pentoxide dissolves in ether producing **blue colouration**. It is actually a peroxo compound having the structure :



Therefore, it is written as $CrO(O_2)_2$ and is also known oxodiperoxochromium (VI).

Learning Plus

Oxidation state of Cr in CrO_5

The structure of CrO_5 shows that it has two peroxo groups. The oxidation state of each peroxo group O_2^{2-} is –2 so that

$x + 1 \times (-2) + 2 \times (-2) = 0$

(for Cr) (for oxygen) (for peroxo)

or $x - 2 - 4 = 0 \quad \therefore x = +6$

Oxidation state of Cr in CrO_5 is +6

(*v*) *H_2O_2 oxidises H_2SO_3 to H_2SO_4*

$$H_2O_2 \longrightarrow H_2O + O$$
$$H_2SO_3 + O \longrightarrow H_2SO_4$$

$$H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$$

or $$\mathbf{SO_3^{2-} + H_2O_2 \longrightarrow SO_4^{2-} + H_2O}$$

(*vi*) *H_2O_2 oxidises sulphides to sulphates*

$$H_2O_2 \longrightarrow H_2O + O] \times 4$$
$$PbS + 4[O] \longrightarrow PbSO_4$$

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

or $$\mathbf{S^{2-} + 4H_2O_2 \longrightarrow SO_4^{2-} + 4H_2O}$$

This property of hydrogen peroxide is quite useful in restoring the original white colour of the lead paintings. *The traces of hydrogen sulphide in the atmosphere blacken the lead paintings due to the formation of lead sulphide (black). To restore the colour of lead paintings, it is dipped in aqueous solution of hydrogen peroxide when the lead sulphide is oxidised to lead sulphate which is white in colour.*

(*vii*) *Hydrogen peroxide oxidises hydrogen sulphide to sulphur and sulphurous acid to sulphuric acid.*

$$H_2S + H_2O_2 \longrightarrow 2H_2O + S$$
$$H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$$

Sulphurous acid — Sulphuric acid

(*viii*) *Hydrogen peroxide oxidises mercury to mercuric oxide in acidic medium.*

$$Hg + H_2O_2 \xrightarrow{\text{dil. } H_2SO_4} HgO + H_2O$$

(*b*) Oxidising action in alkaline solution

Hydrogen peroxide can also accept electrons in the alkaline medium and acts as an oxidising agent.

$$H_2O_2 + OH^- + 2e^- \longrightarrow 3OH^-$$

(*i*) *In alkaline medium, it oxidises manganese sulphate to manganese dioxide.*

$$MnSO_4 + H_2O_2 + 2NaOH \longrightarrow MnO_2 + Na_2SO_4 + 2H_2O$$

Manganese sulphate — Manganese dioxide

$$\mathbf{Mn^{2+} + H_2O_2 + 2OH^- \longrightarrow MnO_2 + 2H_2O}$$

or $$\mathbf{Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-}$$

(*ii*) *In alkaline medium also, H_2O_2 oxidises ferrous ions to ferric ions :*

$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH^-$$

(*iii*) *In alkaline medium, H_2O_2 oxidises chromium salts to chromates*

$$Cr_2(SO_4)_3 + 3H_2O_2 + 10NaOH \longrightarrow 2Na_2CrO_4 + 3Na_2SO_4 + 8H_2O$$

Chromium sulphate — Sod. chromate

or $$\mathbf{2Cr^{3+} + 3H_2O_2 + 10\,OH^- \longrightarrow 2CrO_4^{2-} + 8H_2O}$$

(*iv*) *Hydrogen peroxide oxidises nitrites, sulphites and arsenites to nitrates, sulphates and arsenates respectively in alkaline medium.*

$$NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$$

Sod. nitrite — Sod. nitrate

$$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$$

Sod. sulphite — Sod. sulphate

$$Na_3AsO_3 + H_2O_2 \longrightarrow Na_3AsO_4 + H_2O$$

Sod. arsenite — Sod. arsenate

Reducing nature

Hydrogen peroxide has also a tendency to take up oxygen from strong oxidising agents and thus, acts as a reducing agent.

$$H_2O_2 + O \longrightarrow H_2O + O_2$$

From oxidising agent

It can act as a **reducing agent in acidic as well as basic medium.**

In acidic medium

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

In alkaline medium

$$H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e^-$$

Some important reactions of hydrogen peroxide behaving as a reducing agent are given beolw :

(a) Reducing action in active medium

(*i*) *H_2O_2 reduces acidified potassium permanganate solution to colourless manganese sulphate.* As a result of this reaction, the pink colour of $KMnO_4$ gets discharged.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 3H_2O + 5(O)$$
$$H_2O_2 + O \longrightarrow H_2O + O_2] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + MnSO_4 + 8H_2O + 5O_2$$

or $$\mathbf{2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2}$$

(*ii*) *It reduces acidified potassium dichromate solution.* As a result the orange colour of $K_2Cr_2O_7$ changes to green due to the formation of chromium salt.

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$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$
$$H_2O_2 + O \longrightarrow H_2O + O_2] \times 3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2O_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2$$

or $Cr_2O_7^{2-} + 8H^+ + 3H_2O_2 \longrightarrow 2Cr^{3+} + 7H_2O + 3O_2$

(*iii*) *It reduces manganese dioxide to manganese sulphate in the presence of dil. H_2SO_4.*

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O$$
$$H_2O_2 + O \longrightarrow H_2O + O_2$$

$$MnO_2 + H_2SO_4 + H_2O_2 \longrightarrow MnSO_4 + 2H_2O + O_2$$

(*iv*) *It reduces ozone to dioxygen*

$$O_3 \longrightarrow O_2 + O$$
$$H_2O_2 + O \longrightarrow H_2O + O_2$$
$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

(*v*) *It reduces hypohalous acid to halide ion in acid medium*

$$HOCl(aq) + H_2O_2(aq) \longrightarrow H_3O^+ + Cl^- + O_2$$

(b) Reducing action in alkaline medium

(*i*) *It reduces potassium permanganate to manganese dioxide in alkaline medium*

$$2KMnO_4\,(aq) + 3H_2O_2\,(aq) \longrightarrow 2MnO_2 + 3O_2 + 2H_2O\,(l) + 2KOH(aq)$$

or $2MnO_4^- + 3H_2O_2 \longrightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

(*ii*) *It reduces ferric (Fe^{3+}) salts to ferrous (Fe^{2+}) salts*

$$2Fe^{3+}(aq) + H_2O_2(aq) + 2OH^- \longrightarrow 2Fe^{2+}(aq) + O_2\,(g) + 2H_2O\,(l)$$

(*iii*) *It reduces alkaline potassium ferricyanide to potassium ferrocyanide*

$$2K_3[Fe(CN)_6] + 2KOH \longrightarrow 2K_4[Fe(CN)_6] + H_2O + O$$
$$H_2O_2 + O \longrightarrow H_2O + O_2$$

$$2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$$

Potassium ferricyanide — Pot. ferrocyanide

or $[Fe(CN)_6]^{3-} + 2OH^- + H_2O_2 \longrightarrow [Fe(CN)_6]^{4-} + 2H_2O + O_2$

(*iv*) *The oxides of metals are reduced to metals. For example, silver oxide is reduced to silver*

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

Silver oxide — Silver

However, lead dioxide is reduced to lead monoxide.

$$PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$$

Lead dioxide — Lead monoxide

(*v*) *It reduces halogens to halide ions*

$$Cl_2 + H_2O_2 + 2OH^- \longrightarrow 2Cl^- + 2H_2O + O_2$$

Since hydrogen peroxide can reduce chlorine, it acts as an **anticholor** *in bleaching by destroying the unreacted chlorine.*

Similarly,

$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$

(*vi*) *It reduces hypohalites to halide*

$$NaOBr + H_2O_2 \longrightarrow NaBr + H_2O + O_2$$

Sod. hypobromite

$$CaOCl_2 + H_2O_2 \longrightarrow CaCl_2 + H_2O + O_2$$

Bleaching powder

5. Bleaching action. Hydrogen peroxide acts as a bleaching agent due to the release of nascent oxygen.

$$H_2O_2 \longrightarrow H_2O + O$$

Thus, the bleaching action of hydrogen peroxide is permanent and is due to oxidation. It oxidises the colouring matter to a colourless product.

Colouring matter + O ⟶ Colourless matter

Hydrogen peroxide is used to bleach delicate materials like ivory, silk, wool, feathers, etc.

6. Addition reactions. Hydrogen peroxide adds to alkenes to form glycols.

$$CH_2 = CH_2 + H_2O_2 \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

Ethylene — Ethylene glycol

Uses of Hydrogen Peroxide

1. It is used in industry as a bleaching agent for textiles, paper, pulp, straw, leather, oils, fats, etc.
2. Domestically, it is used as a hair bleach and as a mild disinfectant.
3. It is used in the manufacture of many inorganic compounds such as sodium perborates, and percarbonates which are important constituents of high quality detergents.
4. It is used as an antiseptic for washing wounds, teeth and ears under the name *perhydrol*.
5. It is used for the production of epioxides, propylene oxide and polyurethanes.
6. It is used for the synthesis of hydroquinone, pharmaceuticals (cephalosoporin), food products like tartaric acid.
7. It is used as an antichlor in bleaching.
8. It is used for restoring the colour of lead paintings.
9. It is used for preserving milk, wine and other liquors.
10. Recently, H_2O_2 is used in environmental chemistry such as in pollution control treatment of domestic and industrial effluents; oxidation of cyanides and restoration of aerobic conditions to sewage wastes.

Because of its fast growing uses, there has been tremendous increase in industrial production.

Structure of hydrogen peroxide.

Hydrogen peroxide has a non-planar structure in which two H atoms are arranged in two directions almost perpendicular to each other and to the axis joining the two oxygen atoms.

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The O—O linkage is called peroxide linkage. The structure of H_2O_2 in the gas phase and solid phase are shown in Fig. 9. In the solid phase, the dihedral angle is reduced to 90.2° from 111.5° in the gas phase.

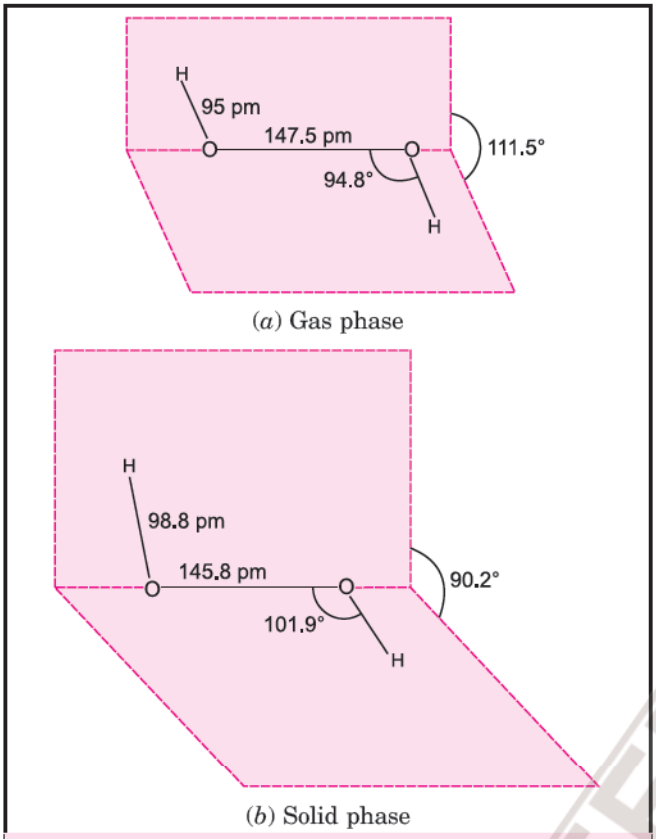

Fig. 9. Structure of H_2O_2 in (a) the gas phase and (b) solid phase (at 110 K).

Strength of hydrogen peroxide

The strength of hydrogen peroxide is expressed in terms of weight or volume as :

(*i*) As weight percentage. The weight percentage of hydrogen peroxide gives the weight of H_2O_2 in 100 g of solution. For example, a 40% solution by wt. means 40 g of hydrogen peroxide are present in 100 g of solution.

(*ii*) As volume. The strength of hydrogen peroxide is commonly expressed as **volume.** This refers **to the volume of oxygen which a solution of H_2O_2 will give.** For example, *a "20 volume" of hydrogen peroxide means that 1 litre of this solution will give 20 litres of oxygen at N.T.P.*

To illustrate this, let us calculate the strength of **20 volume** of hydrogen peroxide in gram per litre.

20 volumes of H_2O_2 means that 1 L of given solution of H_2O_2 will give 20 L of oxygen at N.T.P. Let us calculate the amount of H_2O_2 present in 1 L of H_2O_2 which gives 20 L of oxygen.

H_2O_2 decomposes as :

$$\underset{2 \times 34 = 68\ g}{2H_2O_2} \longrightarrow 2H_2O + \underset{22{,}400\ mL\ at\ N.T.P.}{O_2}$$

According to the equation, 1 mole of oxygen (or 22.4 L of oxygen) at N.T.P. is liberated from 2 mol (or 68 g) of H_2O_2.

22.4 L of oxygen at N.T.P. is produced from $H_2O_2 = 68$ g

1 L of oxygen at N.T.P. is produced from

$$H_2O_2 = \frac{68}{22.4}\ g$$

20 L of oxygen at N.T.P. are produced from

$$H_2O_2 = \frac{68}{22.4} \times 20\ g = \mathbf{60.7\ g}$$

$\therefore$ 1 L of H_2O_2 solution of 20 volume = 60.7 g H_2O_2

Strength of 20 volume H_2O_2 = 60.7 g/litre.

SOLVED EXAMPLES

Example 4.

Calculate the strength and normality of 10 volume solution of hydrogen peroxide. ***N.C.E.R.T.***

Solution: 10 volume H_2O_2 solution means that 1 L of this solution will liberate 10 L of oxygen at N.T.P. Let us calculate the amount of H_2O_2 (in grams) which gives 10 L of oxygen at N.T.P. This amount will be present in 1 L of 10 volume solution of H_2O_2.

H_2O_2 decomposes as :

$$\underset{2 \times 34 = 68\ g}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4\ L\ at\ N.T.P.}{O_2}$$

22.4 L of O_2 at N.T.P. is produced from $H_2O_2 = 68$ g

$$10\ L\ of\ O_2\ at\ N.T.P.\ is\ produced\ from\ H_2O_2 = \frac{68}{22.4} \times 10 = 30.357\ g$$

$\therefore$ Strength of H_2O_2 in 10 volume H_2O_2 = 30.357 g/litre

$$\text{Now, normality} = \frac{\text{Gram equivalents dissolved per litre of solution}}{\text{Gram equivalent of } H_2O_2 \over \text{Volume of solution in litres}}$$

$$\text{Gram equivalents of } H_2O_2 = \frac{30.357}{17} = 1.79$$

(Eq. wt. of H_2O_2 = 17)

$$\text{Normality} = \frac{1.79}{1} = \mathbf{1.79\ N.}$$

Example 5.

Calculate the strength in volumes of a solution containing 30.36 g / litre of H_2O_2.

Solution: Let us calculate the volume of O_2 which is liberated by 30.36 g H_2O_2 at N.T.P. This will correspond to volume strength of H_2O_2.

Hydrogen peroxide decomposes as :

$$\underset{2 \times 34 = 68\ g}{2\ H_2O_2} \longrightarrow 2H_2O + \underset{\text{N.T.P.}}{\overset{22.4\ L\ at}{O_2}}$$

68 g of H_2O_2 produces O_2 at N.T.P. = 22.4 L

30.36 g of H_2O_2 will produce O_2 at N.T.P.

$$= \frac{22.4}{68} \times 30.36 = \mathbf{10\ L}$$

The given solution of H_2O_2 produces 10 L of O_2 at N.T.P.

$\therefore$ Volume strength = **10 volumes.**

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❑ **Example 6.**

Calculate the volume strength of 2N H_2O_2 solution.

Solution: Strength = Normality × Equivalent weight

Normality = 2N, Equivalent weight of H_2O_2 = 17

$\therefore$ Strength = $2 \times 17 = 34$g/L

Hydrogen peroxide decomposes as :

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
$$2 \times 34 = 68g \qquad 22.4\text{L at N.T.P.}$$

68g of H_2O_2 produce O_2 at N.T.P. = 22.4L

34g of H_2O_2 will produce O_2 at N.T.P. $= \frac{22.4 \times 34}{68}$

$= 11.2$ L

The given solution of H_2O_2 produces 11.2L of O_2 at N.T.P.

$\therefore$ Volume strength = **11.2 volumes**

❑ **Example 7.**

What is the mass of hydrogen peroxide present in 1 litre of a 2M solution ? Calculate the volume of oxygen at S.T.P. liberated upon the complete decomposition at 100 cm^3 of the above solution.

Solution: Molecular mass of $H_2O_2 = 2 + 32 = 34$ g

Now, 1 litre of 1 M solution contains $H_2O_2 = 34$ g

$\therefore$ 1 litre of 2 M solution contains $H_2O_2 = 34 \times 2 = 68$ g

H_2O_2 decomposes as :

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
$$2 \times 34 = 68\text{ g} \qquad 22400\text{ cm}^3$$

Mass of H_2O_2 in 100 cm^3 of the solution

$$= \frac{68}{1000} \times 100 = 6.8\text{ g}$$

Now, according to the equation

68 g of H_2O_2 at S.T.P. evolve oxygen = 22400 cm^3

6.8 g of H_2O_2 at S.T.P. evolve oxygen

$$= \frac{22400}{68} \times 6.8 = \mathbf{2240\ cm^3.}$$

❑ **Example 8.**

A 5.0 cm^3 of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at S.T.P.

Solution: H_2O_2 reacts with acidified KI solution as :

$$2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + I_2 + 2H_2O$$
$$34\text{ g} \qquad 254\text{ g}$$
$$5\text{ cm}^3 \qquad 0.508\text{ g}$$

254 g of I_2 is liberated by H_2O_2 = 34 g

0.508 g of I_2 is liberated by $H_2O_2 = \frac{34}{254} \times 0.508$

$= 0.068$ g

5 cm^3 of H_2O_2 contains = 0.068 g

1 cm^3 of H_2O_2 contains $= \frac{0.068}{5} = 0.0136$ g

Now $2H_2O_2 \longrightarrow 2H_2O + O_2$

68 g — 22400 ml at S.T.P.

68 g of H_2O_2 give O_2 at S.T.P. = 22400 ml

1 cm^3 or 0.0136 g of H_2O_2 give O_2 at S.T.P.

$$= \frac{22400}{68} \times 0.0136\text{ g}$$
$$= 4.48\text{ ml of S.T.P.}$$

1 cm^3 of H_2O_2 at S.T.P. gives 4.48 ml of O_2.

$\therefore$ Strength of H_2O_2 = **4.48 volumes.**

❑ **Example 9.**

Calculate the volume strength of a 3% solution of H_2O_2.

Solution: 100 mL of solution contains $H_2O_2 = 3$ g

1000 mL of solution will contain H_2O_2

$$= \frac{3}{100} \times 1000 = 30\text{ g}$$

H_2O_2 decomposes :

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
$$68\text{ g} \qquad 22.4\text{ at N.T.P.}$$

68 g of H_2O_2 give O_2 at N.T.P. = 22.4 L

$\therefore$ 30 g of H_2O_2 will give O_2 at N.T.P.

$$= \frac{22.4}{68} \times 30$$
$$= 9.88\text{ L}$$
$$= 9880\text{ mL}$$

But 30 g of H_2O_2 is present in 1000 mL of H_2O_2

1000 mL of H_2O_2 solution gives O_2 at N.T.P. = 9880 mL

1 mL of H_2O_2 solution will give O_2 at N.T.P.

$$= \frac{9880}{1000} = 9.88\text{ mL}$$

Hence volume strength of 3% H_2O_2 = **9.88**

❑ **Example 10.**

30 mL of H_2O_2 solution after acidification required 30 mL of N/10 $KMnO_4$ solution for complete oxidation. Calculate the percentage and volume strength of H_2O_2 solution.

Solution: To calculate the normality of H_2O_2 solution, apply normality equation,

$$N_1V_1 \equiv N_2V_2$$
$$H_2O_2 \quad KMnO_4$$

For H_2O_2, $V_1 = 30$ mL, $N_1 = ?$

For $KMnO_4$, $V_2 = 30$ mL, $N_2 = \frac{N}{10}$

$$N_1 \times 30 = \frac{N}{10} \times 30$$

$\therefore$ $N_1 = \frac{1}{10} \times \frac{30}{30} = 1/10\text{ N} = 0.1\text{N}$

Strength = Equivalent wt. × Normality

$= 17 \times .01 = 1.7$ g/L

$\therefore$ % of strength $= \frac{1.7}{1000} \times 100 = 0.17\%$

H_2O_2 decomposes as :

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
$$68\text{ g} \qquad 22.4\text{ L at N.T.P.}$$

68 g of H_2O_2 give O_2 at N.T.P. = 22.4L

1.7g of H_2O_2 will give O_2 at N.T.P.

$$= \frac{22.4}{68} \times 1.7 = 0.56\text{ L}$$

Since 1.7g of H_2O_2 is present in 1L,

$\therefore$ Volume strength **= 0.56 volumes**.

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Practice Problems

11. What is the significance of 15 volume of H_2O_2 solution ?

12. What is the trade name of hydrogen peroxide used as an antiseptic ?

13. Does hydrogen peroxide act as
(*i*) strong acid (*ii*) bleaching agent ?

14. Name two compounds which retard the decomposition of hydrogen peroxide.

15. Calculate the normality of 20 volume solution of H_2O_2.

16. Calculate the amount of hydrogen peroxide present in 10 ml of 25 volume solution of H_2O_2.

17. Old paintings of lead are generally washed with dilute solution of hydrogen peroxide in order to regain its colour. Why ?

18. 10 ml of given H_2O_2 solution contains 0.91 g of H_2O_2. Express its strength in volumes.

19. Calculate the volume strength of 1.6 N H_2O_2 solution.

Answers to Practice Problems

11. It means that 1 L of this solution gives 15 L of oxygen at N.T.P.

12. Perhydrol.

13. (*i*) weak acid (*ii*) yes

14. acetanilide, glycerol.

15. 20 volume of H_2O_2 solution means that 1L of this solution will liberate 20L of O_2 at N.T.P.

$2H_2O_2 \longrightarrow 2H_2O + O_2$
68g 22.4 at N.T.P.

22.4L of O_2 at N.T.P. is produced from H_2O_2 = 68 g
20L of O_2 at N.T.P. is produced from H_2O_2

$$= \frac{68}{22.4} \times 20 = 60.71\text{g}$$

Strength of H_2O_2 = 60.71 g/L

$$\text{Gram equivalents of } H_2O_2 = \frac{60.71}{17} = 3.57$$

$$\therefore \text{Normality} = \frac{3.57}{1} = \mathbf{3.57\ N}$$

16. $2H_2O_2 \longrightarrow 2H_2O + O_2$
68 g 22.4L at N.T.P.

22.4L of O_2 at N.T.P. is produced from H_2O_2 = 68 g
25 L of O_2 at N.T.P. is produced from H_2O_2

$$= \frac{68}{22.4} \times 25 = 75.9\text{ g}$$

Strength of 25 volume H_2O_2 = 75.9 g/L

$$\text{Amount of } H_2O_2 \text{ present in 10 mL} = \frac{75.9}{1000} \times 10$$
$$= \mathbf{0.759\ g.}$$

17. Black colour in paintings is due to lead sulphide (PbS). This is oxidised to lead sulphate by hydrogen peroxide.

18. $2H_2O_2 \longrightarrow 2H_2O + O_2$
68g 22.4 L at N.T.P.

$$\text{Amount of } H_2O_2 \text{ in 1L} = \frac{0.91 \times 1000}{10} = 91\text{ g}$$

68g of H_2O_2 give O_2 at N.T.P. = 22.4 L

$$\text{91g of } H_2O_2 \text{ will give } O_2 \text{ at N.T.P.} = \frac{22.4}{68} \times 91$$
$$= 30$$

Since 91 g of H_2O_2 is present in 1L,
$\therefore$ Volume strength = **30 volume**

19. Strength of H_2O_2 = 1.6 × 17 = 27.2g/L
68g of H_2O_2 produce O_2 at N.T.P. = 22.4 L
27.2 g of H_2O_2 will produce O_2 at N.T.P.

$$= \frac{22.4}{68} \times 27.2 = 8.96\text{L}$$

The given solution of H_2O_2 produces 8.96L of O_2 at N.T.P.
$\therefore$ Volume strength = **8.96 volume.**

LIQUID HYDROGEN AS A FUEL

Fuels burn to release large quantities of energy.

The energy released by combustion of fuels such as dihydrogen, methane, LPG and gasoline (octane) as compared in terms of the same amounts in mole, mass and volume are given in Table 8.

It is clear from the above table that on mass to mass basis, dihydrogen can release more energy than even gasoline *i.e.*, octane (about three times). Moreover, the pollutants in the combustion of dihydrogen will be less than petrol. The only pollutant will be oxides of dinitrogen (due to the presence of impurity with dihydrogen). However, this can be reduced by injecting small amounts of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not occur.

Liquid hydrogen is used as an important rocket fuel. A primary condition for a rocket fuel is that its mass be as small as possible for a given amount of energy produced. Since hydrogen has low mass and high enthalpy of combustion, therefore, it was considered as an ideal rocket fuel. It was used in

Table 8 Energy released by combustion of various fuels in moles, mass and volume

Energy released on combustion (kJ)	Dihydrogen (in gaseous state)	Dihydrogen (in liquid state)	LPG	CH_4 gas	Octane (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

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Saturn–V rocket that enabled the first astronauts to land on the moon and it has been the main fuel in the space shuttle rockets. Both the hydrogen and the oxygen needed to burn the hydrogen are carried on the rocket in liquid form.

The important **advantages** of hydrogen as a fuel for rockets are :

1. It releases greater energy per unit weight of the fuel.
2. The only product of combustion is water.
3. There is no emission of environmental pollutants such as CO, CO_2, SO_2, oxides of nitrogen (NO_x), hydrocarbons, aldehydes and lead compounds, etc.
4. Internal combustion engines can easily be modified for use of hydrogen as fuel.
5. Fuel cells for generation of electric power with conversion efficiency of 70–85% have been successfully operated commercially.

Hydrogen is so abundant in the form of water in the oceans that it could meet all our energy needs, and provide inexhaustible supply. However the main problem is to extract it from water. This is because decomposition of water to hydrogen and oxygen :

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2} O_2(g) \quad \Delta H = 286 \text{ kJ}.$$

requires 286 kJ per mole of water. Therefore it has been difficult to carry out this reaction economically. Because of large amount of electricity required, electrolysis is an expensive method. It can be carried out only where electricity is cheap.

However, the main **problems for the use of hydrogen** as a fuel are :

(*i*) Hydrogen is highly combustible and is difficult to handle safely. Because of its combustible nature, it burns with explosion.

(*ii*) It is not easy to store or transport hydrogen safely and compactly from one place to another. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Moreover, dihydrogen gas is converted into liquid state by cooling to 20 K. This would require expensive insulated tanks.

Tanks made of metal alloys like Ti—TiH_2, Mg—MgH_2, $NaNi_5$, etc. are in use for storage of dihydrogen in small quantities.

(*iii*) It is an expensive fuel because cost of production is high.

HYDROGEN ECONOMY

With the growth of modern civilization, the need of energy has been continuously increasing at a very fast rate. The natural reserves of the world for energy such as coal and oil are finite. The continuous use of these sources may exhaust them completely and this may cause a serious problem for getting energy. The nuclear power can also not meet all our energy requirements, particularly for small mobile units such as cars, etc. The search for alternative sources of energy has given a solution as **"hydrogen economy" whereby *energy is transported and stored in the form of liquid or gaseous hydrogen. Hydrogen is considered to be a possible source of clean energy.*** The advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. The major problem is to make hydrogen cheaply. Various methods of obtaining hydrogen are being explored.

If the problems of its safety and its economically production are solved, it may eventually be delivered to homes and industry by pipelines as natural gas. Hydrogen might even be used as fuel to run vehicles and jet planes and produce electricity. For this purpose it might be stored as a liquid at very low temperature or as solid metal hydride that when heated decomposes to produce hydrogen.

Better ways of storing hydrogen are worked out. In USA, technology exists for producing hydrogen electrically and storing it in bulk. For example, large quantities of liquid hydrogen are routinely stored in vacuum insulated cryogenic tanks for US space programme. It can also be stored in underground tanks and transported by pipelines. Smaller storage units made of metal alloys like Ti-TiH_2, $NaNi_5$, Mg-MgH_2, etc. are used. The advantages for hydrogen to be used as an automobile fuel are the larger energy released per unit mass of fuel and the absence of emission of pollutants such as CO, CO_2, oxides of nitrogen, SO_2, hydrocarbons and lead compounds. The product of combustion is only water. Several conventional internal combustion petrol engines have already been modified to run on hydrogen.

It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially about 5% dihydrogen has been mixed with CNG for use in four wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, hydrogen is also used in fuel cells for the generation of electric power.Fuel cells using hydrogen for the generation of electricity have been successfully operated with a conversion efficiency of about 70–85%.

The production of non-electrolytic hydrogen is drawing the attention of many scientists in recent years. The main principle involved in the process is the mode of transferring free energy to a water molecule for decomposing it. Fortunately, some success has been achieved in this field and it is expected that it will be possible to develop economically viable and safe sources of hydrogen for its use as a general source of energy in future.

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add on

Conceptual Questions

CONCEPTUAL QA

Q. 1. Which isotope of hydrogen is used commoly as a tracer in organic reactions ?

Ans. Both deuterium and tritium can be used as tracers in organic reactions. However, tritium is not only radioactive but is also least abundant hydrogen isotope and therefore, deuterium is commonly used as tracer to study the mechanism of organic reactions.

Q. 2. Why is dihydrogen gas not preferred in balloons ?

Ans. Dihydrogen gas is combustible in nature. Therefore, it may react with oxygen highly violently. Thus, it is not used in balloons.

Q. 3. Acetanilide checks the decomposition of H_2O_2. What is this compound called ?

Ans. Acetanilide is a neutral compound which suppresses the decomposition of H_2O_2 into H_2O and O_2. It is called an inhibitor.

Q. 4. Consider the reaction of water with F_2 and suggest, in terms of oxidation and reduction which species are oxidised or reduced.

Ans. $2F_2(g) + 2H_2O(aq) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$

In this reaction, water is oxidised to oxygen by F_2. Fluorine has been reduced to F^- ion.

Q. 5. What is meant by autoprotolysis of water ?

Ans. Autoprotolysis is a reaction in which two same molecules react to give ions with proton transfer. For example, in water, a proton from one H_2O molecule is transferred to another water molecule leaving behind OH^- ion and forming a H_3O^+ ion.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Q. 6. How will you prepare a sample of ND_3 ?

Ans. ND_3 is prepared by reacting magnesium nitride (Mg_3N_2) with heavy water as :

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$

Q. 7. Classify the following as covalent, ionic or polymer interstitial hydrides :
(*i*) BeH_2 (*ii*) CaH_2 (*iii*) RbH (*iv*) GeH_4 (*v*) TiH_2

Ans.

(*i*)	BeH_2	:	Polymeric [exists as $(BeH_2)_n$]
(*ii*)	CaH_2	:	Ionic
(*iii*)	RbH	:	Ionic
(*iv*)	GeH_4	:	Covalent
(*v*)	TiH_2	:	Interstitial

Q. 8. Name the radioactive isotope of hydrogen.

Ans. Tritium (^3_1T).

Q. 9. Give one example of a reaction in which dihydrogen acts as a reducing agent and an oxidising agent.

Ans. (*i*) Dihydrogen acts as a reducing agent :

$$CuO + H_2 \longrightarrow Cu + H_2O$$

(*ii*) Dihydrogen acts as an oxidising agent :

$$2Na + H_2 \longrightarrow 2NaH$$

Q. 10. How is heavy water obtained from ordinary water ?

Ans. Heavy water is obtained from ordinary water by repeated electrolysis in the presence of 3% NaOH.

Q. 11. Name one compound in which hydrogen occurs as (i) +1 and (ii) –1 oxidation state.

Ans. (*i*) +1 in HCl

(*ii*) –1 in NaH

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CONCEPTUAL QA

Q. 12. What type of elements form interstitial hybrides ?

Ans. Elements of *d*– and *f*– block.

Q.13. Which of the two is heavier 1 kg of ice or 1 kg of water?

Ans. Both have same weight.

Q.14. Among NH_3, H_2O and HF, which would you expect to have highest magnitude of hydrogen bonding and why ?

Ans. HF will have maximum hydrogen bonding because it has highest electronegativity among N, O and F.

Q.15. Complete the following equations :

(*i*) $Fe\ (s) + H_2O\ (g) \longrightarrow$

(*ii*) $PbS\ (s) + H_2O_2\ (aq) \longrightarrow$

(*iii*) $MnO_4^-\ (aq) + H_2O_2\ (aq) \longrightarrow$

Ans. (*i*) $3Fe\ (s) + 4H_2O\ (g) \longrightarrow Fe_3O_4\ (s) + 4H_2\ (g)$

(*ii*) $PbS\ (s) + 4H_2O_2\ (aq) \longrightarrow PbSO_4\ (s) + 4H_2O$

(*iii*) $2MnO_4^-\ (aq) + 5H_2O_2\ (aq) + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

Q.16. Complete the following reactions :

(*i*) $CuO\ (s) + H_2\ (g) \longrightarrow$

(*ii*) $CO\ (g) + H_2\ (g) \longrightarrow$

Ans. (*i*) $CuO\ (s) + H_2\ (g) \longrightarrow H_2O + Cu$

(*ii*) $CO\ (g) + 2H_2\ (g) \xrightarrow[\text{Catalyst}]{\text{Cobalt}} CH_3OH\ (l)$

Q.17. Give an example each of an ionic hydride and a covalent hydride.

Ans. Ionic hydride : NaH

Covalent hydride : NH_3

Q.18. How many hydrogen bonded water molecule(s) are present in $CuSO_4.5H_2O$? ***N.C.E.R.T.***

Ans. In $CuSO_4.5H_2O$, there is one hydrogen bonded water molecule which is outside the coordination sphere. The other four molecules of water are coordinated.

Q.19. Complete the following reactions :

(*i*) $CaO\ (s) + H_2O\ (l) \longrightarrow$

(*ii*) $Na_2O\ (s) + H_2O\ (l) \longrightarrow$

Ans. (*i*) $CaO\ (s) + H_2O\ (l) \longrightarrow Ca(OH)_2\ (aq)$

(*ii*) $Na_2O\ (s) + H_2O\ (l) \longrightarrow 2NaOH\ (aq)$

Q.20. What happens when heavy water is added to calcium carbide ?

Ans. Deutero acetylene is formed

$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$.

Chapter Summary

Key Terms

- **Coal gasification.** The process of producing a mixture of carbon monoxide and hydrogen from coal.
- **Softening of water.** The process of the removal of hardness from water.
- **Zeolites.** Hydrated sodium aluminium silicates $Na_2\ Al_2\ Si_2\ O_8\ .\ x\ H_2O$.

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CHAPTER ROUND UP

HYDROGEN

- Hydrogen is the first element in the periodic table.
- It has atomic number 1 and its electronic configuration is $1s^1$.
- Hydrogen resembles alkali metals as well as halogens in its properties.
- Hydrogen exists in three isotopes *i.e.*, protium (^1_1H), deuterium (^2_1H or D) and tritium (^3_1H or T). Tritium is radioactive and emits β-particles ($t_{1/2}$ = 12.33 years).
- Electrolysis of an aqueous solution of HCl liberates H_2 at the cathode and the electrolysis of NaH (fused) liberates H_2 at the anode.
- Ordinary hydrogen exists as *ortho* and *para* hydrogen. The nuclei of ortho hydrogen spin in the same direction while that of para hydrogen spin in the opposite directions.
- At room temperature, the ratio of ortho to para hydrogen is 3 : 1, at the temperature of liquefaction of air, the ratio is 1 : 1 and at 0 K, hydrogen contains mainly para hydrogen, which is more stable.
- Alkali metals and alkaline earth metals react with cold water evolving H_2 gas.
- Mg, Zn and Al decompose boiling water evolving H_2 gas while Fe decomposes steam producing H_2 gas.
- Hydrogen forms compounds by losing, gaining or sharing of electrons and exhibits oxidation states of +1, −1 and 0.
- Hydrogen reacts with metals and non-metals

$$2Na + H_2 \longrightarrow 2NaH$$
$$N_2 + 3H_2 \longrightarrow 2NH_3$$
$$H_2 + X_2 \longrightarrow 2HX \qquad (X = F, Cl, Br, I \text{ and reactivity of halogen is } F_2 > Cl_2 > Br_2 > I_2)$$

- Hydrogen acts as a powerful reducing agent and reduces CuO, ZnO, PbO, Fe_3O_4 etc.

$$ZnO + H_2 \longrightarrow Zn + H_2O$$

HYDRIDES

- **Ionic :** formed by combination of H with highly electropositive metals.
  e.g. LiH, KH, CaH_2, SrH_2
- **Molecular or covalent :** formed by combination of elements of higher electronegativity.
  e.g. HF, H_2O, NH_3, B_2H_6, CH_4, H_2S, PH_3
- **Interstitial:** formed by elements of *d*- and *f*-block.
  e.g. $ZrH_{1.9}$, $TiH_{1.73}$, $LaH_{2.76}$
- **Complex :** $LiAlH_4$, $NaBH_4$

Hydrolith is the common name of CaH_2.

HYDROGEN PEROXIDE

- It is prepared in the laboratory as

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$
$$BaO_2.8H_2O(s) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + H_2O_2 + 8H_2O$$

- On commercial scale, it is prepared by
  − electrolysis of 50% H_2SO_4 solution
  − 2-Ethyl anthraquinol
- H_2O_2 decomposes as

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

  Its decomposition is retarded by adding glycerol, phosphoric acid or acetanilide (negative calalysts).
- H_2O_2 is a weak acid and forms two types of salts.

$$\text{e.g.} \quad NaOH + H_2O_2 \longrightarrow NaHO_2 + H_2O$$
$$2NaOH + H_2O_2 \longrightarrow Na_2O_2 + 2H_2O$$

- H_2O_2 acts as an oxidizing agent as well as a reducing agent in both acidic and basic medium.
- The bleaching action of H_2O_2 is due to **oxidation** and is **permanent**.

WATER

- Water is angular or bent molecule and H−O−H bond is 104.5°
- Water can act as a base towards acids stronger than itself and as an acid towards bases stronger than it.
- Water which produces lather with soap solution readily is called **soft water**.
- Water which does not produce lather with soap solution readily is called **hard water**.
- The hardness of water is due to the presence of the bicarbonates, chlorides and sulphates of calcium and magnesium.
- Water acts as an oxidising agent towards highly active metals and itself gets reduced to H_2.

$$2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$$

  It acts as a reducing agents towards highly electronegative elements and itself gets oxidised to O_2 or O_3.

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$$
$$\text{e.g.} \quad 2F_2 + 2H_2O \longrightarrow 4H^+ + 4F^- + O_2$$
$$\text{or} \quad 3F_2 + 3H_2O \longrightarrow O_3 + 6H^+ + 6F^-$$

- In $CuSO_4 \cdot 5H_2O$, Cu is coordinated to four H_2O molecules while the fifth H_2O molecule is hydrogen bonded to SO_4^{2-} ion.

HEAVY WATER

- Heavy water is D_2O which is obtained by prolonged hydrolysis of water or by fractional distillation.
- The reactions of D_2O are slower than those of H_2O.
- D_2O is used in nuclear reactors as a moderator

Strength of H_2O_2

- Strength of hydrogen peroxide is usually expressed as **volume**. For example, a 20 volume H_2O_2 means that 1 litre of this solution will give 20 litres of oxygen at N.T.P.
- Strength of 10 volume H_2O_2 = 30.35 g/L
- Normality of 10 volume H_2O_2 = 1.79 N
- Molarity of 10 volume H_2O_2 = 0.89 M

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NCERT FILE Solved

NCERT Textbook Exercises

Q.1. Justify the position of hydrogen in the periodic table on the basis of its electronic configuration.

Ans. *Refer Text Page 1.*

Q.2. Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes ?

Ans. Protium, $^{1}_{1}H$, deuterium $^{2}_{1}H$ or D, tritium $^{3}_{1}H$ or T. Mass ratio of protium, deuterium and tritium = 1 : 2 : 3.

Q.3. Why does hydrogen occur in a diatomic form rather than in a monoatomic form under normal conditions ?

Ans. Hydrogen atom has only one electron in its valence shell ($1s^1$) and has only one electron less than the stable noble gas configuration of helium. Therefore, it shares its single electron with electron of other H-atom to achieve stable inert gas configuration of He. Therefore, it readily forms diatomic molecule and exists as H_2 rather than monoatomic.

Q. 4. How can the production of dihydrogen, obtained from 'coal gasification', be increased ?

Ans. The process of producing a mixture of carbon monoxide and hydrogen from coal is called coal gasification. This mixture is also called synthesis gas or syn gas.

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

The production of hydrogen can be increased by reacting carbon monoxide of syn gas with steam in the presence of iron chromate as catalyst at 673K.

$$\underset{\text{steam}}{CO(g) + H_2O(g)} \xrightarrow[673K]{FeCrO_4} CO_2(g) + H_2(g)$$

The CO_2 thus produced is removed by scrubbing with a solution of sodium arsenite.

Q. 5. Describe the bulk preparation of dihydrogen by electrolytic method. What is the role of an electrolyte in this process ?

Ans. *Refer Text Page 6.*

Q. 6. Complete the following reactions :

(*i*) $H_2(g) + M_mO_o(s) \xrightarrow{\Delta}$

(*ii*) $CO(g) + H_2(g) \xrightarrow[\text{Catalyst}]{\Delta}$

(*iii*) $C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{Catalyst}]{\Delta}$

(*iv*) $Zn(s) + NaOH(aq) \xrightarrow{\text{Heat}}$

Ans. (*i*) $H_2(g) + M_mO_o(s) \xrightarrow{\Delta} mM(s) + oH_2O(l)$

(*ii*) $CO(g) + 2H_2(g) \xrightarrow[\text{Catalyst}]{\Delta} \underset{\text{Methanol}}{CH_3OH(l)}$

(*iii*) $C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{Catalyst}]{\Delta} 3CO(g) + 7H_2(g)$

(*iv*) $Zn(s) + 2NaOH(aq) \xrightarrow{\text{Heat}} \underset{\text{Sodium zincate}}{Na_2ZnO_2(aq)} + H_2(g)$

Q. 7. Discuss the consequences of high enthalpy of H—H bond in terms of chemical reactivity of dihydrogen.

Ans. The bond dissociation enthalpy of H—H bond is very high (435.9 kJ mol^{-1}). Due to high bond enthalpy, it is not very reactive at room temperature. However, at high temperatures or in the presence of catalysts, hydrogen combines with many metals and non-metals to form hydrides.

Q. 8. What do you understand by (*i*) electron-deficient, (*ii*) electron-precise, and (*iii*) electron-rich compounds of hydrogen? Provide justification with suitable examples.

Ans. (*i*) Electron deficient hydrides are those which donot have sufficient number of electrons to form normal covalent bonds. For example, hydrides of group 13 (BH_3, AlH_3, etc). To make up their deficiency they generally exist in polymeric forms such as B_2H_6, Al_2H_6, etc.

(*ii*) Electron precise hydrides are those which have sufficient number of electrons required for forming covalent bonds. For example, hydrides of group 14 (CH_4, SiH_4, GeH_4, SnH_4, PbH_4 etc). These have tetrahedral shapes.

(*iii*) Electron rich hydrides are those which have excess electrons as required to form normal covalent bonds. For example, hydride of group 15 or 17 (*i.e.*, NH_3, PH_3, H_2O, H_2S, H_2Se, H_2Te, etc). The excess electrons in these hydrides are present as lone pairs.

Q. 9. What characteristics do you expect from an electron-deficient hydride with respect to its structure and chemical reactions ?

Ans. Electron deficient hydrides donot have sufficient number of electrons to form normal covalent bonds. Therefore, to make up their deficiency, they generally exist as polymeric species *e.g.*, B_2H_6, B_4H_{10}, $(AlH_3)_n$ etc.

The electron deficient hydrides act as electron acceptors *i.e.*, Lewis acids and thus form complexes with Lewis bases. For example :

$$\underset{\text{Diborane}}{B_2H_6} + \underset{\substack{\text{Trimethylamine}\\\text{(Lewis base)}}}{2NMe_3} \longrightarrow 2BH_3 \longleftarrow NMe_3$$

$$\underset{\text{Diborane}}{B_2H_6} + \underset{\substack{\text{Carbon monoxide}\\\text{(Lewis base)}}}{2CO} \longrightarrow 2BH_3 \longleftarrow CO$$

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Q. 10. Do you expect the carbon hydrides of the type (C_nH_{2n+2}) to act as 'Lewis' acid or base ? Justify your answer.

Ans. Carbon hydrides of the type C_nH_{2n+2} are electron precise hydrides. They have exact number of electrons required to form covalent bonds. Therefore, they have no tendency to either gain or lose electrons and hence they do not act as Lewis acids or Lewis bases.

Q. 11. What do you understand by the term "non-stoichiometric hydrides" ? Do you expect this type of the hydrides to be formed by alkali metals ? Justify your answer.

Ans. The hydrides in which the ratio of the metal to hydrogen is fractional and does not correspond to actual formula are called **non-stoichiometric hydrides**. Their composition varies with temperature and pressure. For example, the hydrides of titanium or zirconium are represented as Ti H_x (x = 1.8 to 2) and Zr H_x (x = 1.30 to 1.75) respectively. This type of hydrides are formed by elements of *d*-and *f*-block.

Alkali metals are very strong reducing agents and they transfer their lone electron to H-atom to form H^- ion. In other words, alkali metal hydrides are ionic in which H^- ions occupy holes of lattice. Since hydride ion is formed by the transfer of an electron, therefore, the ratio of metal to hydrogen is always fixed and hence alkali metals form only stoichiometric hydrides. Thus, alkali metals donot form non-stoichiometric hydrides.

Q. 12. How do you expect the metallic hydrides to be useful for hydrogen storage ? Explain.

Ans. Metallic hydrides can be used as hydrogen storage. This is because in metallic hydrides, hydrogen is absorbed as H-atoms. Due to inclusion of H-atoms, the metal lattice expands and therefore becomes less stable. Therefore, when metallic hydride is heated, it decomposes to form hydrogen and very finely divided metal.

The hydrogen thus produced can be used as a fuel. Thus transition metals or their alloys can be used to store and transport hydrogen to be used as a fuel. This is called hydrogen economy.

Q. 13. How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes ? Explain.

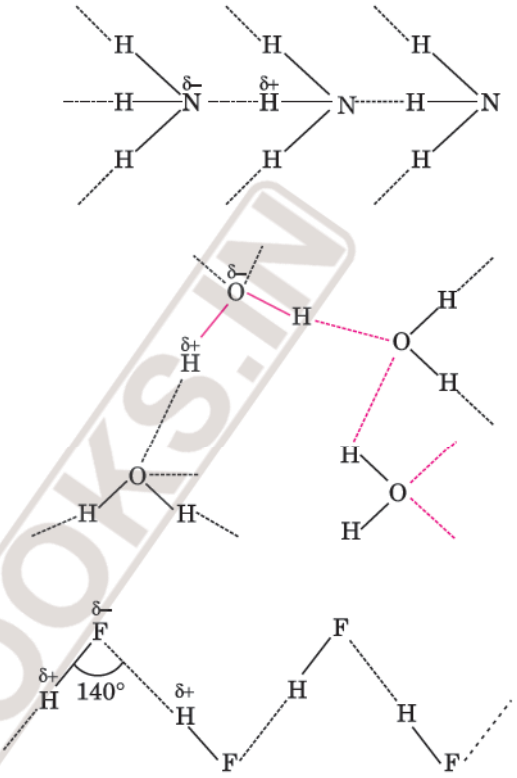
Ans. Atomic hydrogen is produced when molecular hydrogen is passed through an electric arc struck between tungsten electrodes at 3773-4273K.

$$H_2 \xrightarrow[3773-4273K]{\text{Electric arc}} 2H \qquad \Delta H = 435.9 \text{ kJ mol}^{-1}$$

The life time of atomic hydrogen is very very small (only 0.3 sec) and hence it immediately gets converted into molecular form by liberating a large amount of energy which may be used for cutting or welding purposes in the form of atomic hydrogen torch. (See page 9).

Q. 14. Among NH_3, H_2O and HF, which would you expect to have highest magnitude of hydrogen bonding and why ?

Ans. All these molecules undergo hydrogen bonding due to greater electronegativity of N, O and F.



Since F is most electronegative and therefore, the magnitude of negative charge on F and positive charge on H will be highest and therefore, H-bonding will be strongest in HF.

Q. 15. Saline hydrides are known to react with water violently producing fire. Can CO_2, a well known fire extinguisher, be used in this case ? Explain.

Ans. Saline hydrides (*e.g.*, NaH, CaH_2 etc) react with water violently to form corresponding metal hydroxide with the evolution of dihydrogen as,

$$NaH(s) + H_2O\ (l) \longrightarrow NaOH\ (aq) + H_2(g)$$

$$CaH_2(s) + 2H_2O\ (l) \longrightarrow Ca(OH)_2\ (aq) + 2H_2(g)$$

These reactions are very exothermic and the evolved H_2 catches fire. The fire produced cannot be extinguished by CO_2 because it gets reduced by hot metal hydride.

$$NaH + CO_2 \longrightarrow HCOONa$$

However, sand is used because it is highly stable solid.

Q. 16. Arrange the following

(*i*) CaH_2, BeH_2 and TiH_2 in order of increasing electrical conductance.

(*ii*) LiH, NaH and CsH in order of increasing ionic character.

(*iii*) H—H, D—D and F—F in order of increasing bond dissociation enthalpy.

(*iv*) NaH, MgH_2 and H_2O in order of increasing reducing property.

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Ans. (*i*) $BeH_2 < CaH_2 < TiH_2$
(*ii*) $LiH < NaH < CsH$
(*iii*) F—F < H—H < D—D
(*iv*) $H_2O < MgH_2 < NaH$

Q. 17. Compare the structures of H_2O and H_2O_2

Ans. In water, O atom is sp^3 hybridised and there are two O—H bonds and two sp^3 hybrid orbitals occupy lone pairs of electrons. Due to stronger lone pair–lone pair repulsions than bond pair–bond pair repulsions, the HOH bond decreases from 109.5° to 104.5°. Therefore, water molecule is a bent or angular molecule. H_2O_2 has non-planar structure. In this structure, two O—O oxygen atoms are bonded to each other by a single covalent bond and each O atom is further bonded to a hydrogen atom by a single covalent bond. The two O—H bonds are in different planes. The dihedral angle between two planes is 111.5° in the gas phase (Fig. 9).

Q. 18. What do you understand by the term 'auto-protolysis' of water ? What is its significance ?

Ans. Auto-protolysis is a reaction in which two same molecules react to give ions with proton transfer. For example, in water, a proton from one water molecule is transferred to another water molecule leaving behind OH^- ions and forming H_3O^+ ion :

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Because of auto-protolysis, water is amphoteric in nature *i.e.,* it reacts with acids as well as bases. It acts as a base towards acids stronger than itself and as an acid towards bases stronger than itself. For example :

$$\underset{\text{acid}_1}{H_2O(l)} + \underset{\text{base}_2}{NH_3(aq)} \longrightarrow \underset{\text{acid}_2}{NH_4^+(aq)} + \underset{\text{base}_1}{OH^-(aq)}$$

$$\underset{\text{base}_1}{H_2O(l)} + \underset{\text{acid}_2}{H_2S(aq)} \longrightarrow \underset{\text{acid}_1}{H_3O^+(aq)} + \underset{\text{base}_2}{HS^-(aq)}$$

It helps to understand Bronsted concept of conjugate acid-base pairs.

Q. 19. Consider the reaction of water with F_2 and suggest, in terms of oxidation and reduction, which species are oxidised/reduced.

Ans. $\underset{\text{Oxidant}}{2F_2(g)} + \underset{\text{Reductant}}{2H_2O(l)} \longrightarrow O_2(g) + 4H^+(aq) + 4F^-(aq)$

or $\underset{\text{Oxidant}}{3F_2(g)} + \underset{\text{Reductant}}{3H_2O(l)} \longrightarrow O_3(g) + 6H^+(aq) + 6F^-(aq)$

Water acts as a reducing agent and gets oxidised to O_2 or O_3.

F_2 acts as an oxidising agent and itself gets reduced to F^-.

Q. 20. Complete the following chemical reactions.

(*i*) $PbS(s) + H_2O_2(aq) \longrightarrow$

(*ii*) $MnO_4^-(aq) + H_2O_2(aq) \longrightarrow$

(*iii*) $CaO(s) + H_2O(g) \longrightarrow$

(*iv*) $AlCl_3(g) + H_2O(l) \longrightarrow$

(*v*) $Ca_3N_2(s) + H_2O(l) \longrightarrow$

Classify the above into (*a*) hydrolysis, (*b*) redox and (*c*) hydration reactions.

Ans. (*i*) $PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$

(*ii*) $MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$

(*iii*) $CaO(s) + H_2O(g) \longrightarrow Ca(OH)_2(aq)$

(*iv*) $AlCl_3(g) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3HCl(aq)$

(*v*) $Ca_3N_2(s) + 6H_2O(l) \longrightarrow 3Ca(OH)_2(aq) + 2NH_3(aq)$

Q. 21. Describe the structure of the common form of ice.

Ans. Ice has a three dimensional network in which each O atom is tetrahedrally surrounded by four hydrogen atoms; two by covalent bonds and two by hydrogen bonds. Ice has open structure having a number of vacant spaces. *Refer Fig. 5 (Page 16).*

Q. 22. What causes the temporary and permanent hardness of water ?

Ans. The temporary hardness is due to the presence of bicarbonates of calcium and magnesium *i.e.,* $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ in water. On the other hand, permanent hardness is caused by the presence of chlorides and sulphates of calcium and magnesium *i.e.,* $CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$ in water.

Q. 23. Discuss the principle and method of softening of hard water by synthetic ion-exchange resins.

Ans. *Refer Text; Page 21.*

Q. 24. Write chemical reactions to show the amphoteric nature of water.

Ans. Water is amphoteric in character and it behaves both as an acid as well as a base. With acids stronger than itself (*e.g.,* H_2S) it behaves as a base and with bases stronger than itself (*e.g.,* NH_3) it acts as an acid.

(*i*) **As a base**

$$\underset{\text{base}_1}{H_2O(l)} + \underset{\text{acid}_1}{H_2S(aq)} \longrightarrow \underset{\text{acid}_2}{H_3O^+(aq)} + \underset{\text{base}_2}{HS^-(aq)}$$

(*ii*) **As an acid**

$$\underset{\text{acid}_1}{H_2O(l)} + \underset{\text{base}_1}{NH_3(aq)} \longrightarrow \underset{\text{acid}_2}{NH_4^+(aq)} + \underset{\text{base}_2}{OH^-(aq)}$$

Q. 25. Write the chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.

Ans. Hydrogen peroxide behaves both as an oxidising agent as well as reducing agent both in acidic and alkaline medium. The oxidation state of O in H_2O_2 is –1. Therefore, it can be oxidised to O_2(zero oxidation state) or reduced to H_2O or OH^- (–2 oxidation state). Some reactions of H_2O_2 are :

(*i*) Oxidising action in acidic medium.

$$2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O$$

(*ii*) Oxidising action in basic medium.

$$Mn^{2+}(aq) + H_2O_2(aq) + 2OH^- \longrightarrow MnO_2(s) + 2H_2O(l)$$

(*iii*) Reducing action in acidic medium

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

(*iv*) Reducing action in basic medium

$$2Fe^{3+}(aq) + H_2O_2(aq) + 2OH^-(aq) \longrightarrow 2Fe^{2+}(aq) + O_2(g) + 2H_2O_2(l)$$

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Q. 26. What is meant by 'demineralised' water and how can it be obtained ?

Ans. Water which is free from all cations and anions is called **demineralised water.** It is obtained by passing hard water first through cation exchange resin and then through anion exchange resin. For detail, *Refer Text (Page 21)*.

Q. 27. Is demineralised or distilled water useful for drinking purposes ? If not, how can it be made useful?

Ans. Demineralised or distilled water is not useful for drinking purposes since it does not contain even useful minerals. Therefore, to make water useful for drinking purposes, useful minerals in proper amounts should be added to demineralised or distilled water.

Q. 28. Describe the usefulness of water in biosphere and biological systems.

Ans. Water is essential to all forms of life. Water constitutes about 65% of the body weight of animals and plants and is essential for their growth. We can live without food for some days but cannot live without water. It is also a principal constituent of earth's surface. In comparison to other liquids, it has characteristic properties such as high specific heat, thermal conductivity, dipole moment, surface tension, dielectric constant, etc. which make water to play a key and significant role in biosphere. The high heat of vaporisation and heat capacity help it for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of minerals and other nutrients for plant and animal metabolism. This also plays an important role in photosynthesis in plants which releases oxygen in the atmosphere.

Q. 29. What properties of water make it useful as a solvent ? What types of compound can it (*i*) dissolve, and (ii) hydrolyse ?

Ans. Water has a high dielectric constant (78.39) and high dipole moment (1.84D). Because of these properties water has the capacity to dissolve most of the inorganic substances, ionic as well as covalent and is, therefore, regarded as a universal solvent. Ionic compounds dissolve in water due to ion-dipole interactions or solvation of ions whereas covalent compounds such as urea, glucose, amines, alcohols, sugar, etc. dissolve in water due to hydrogen bonding.

Water can easily hydrolyse many ionic and covalent compounds of metals and non-metals. In these reactions, H^+ and OH^- ions of water interact with anions and cations of compounds to form acids and bases. For exmaple,

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$
$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$
$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$
$$CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$$
$$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + \underset{\text{acetylene}}{C_2H_2}$$

For more reactions, *Refer Text*.

Q. 30. Knowing the properties of H_2O and D_2O, do you think that D_2O can be used for drinking purposes?

Ans. Heavy water is injurious to plants, animals and human beings because it slows down the rates of reactions occurring in them. Thus, heavy water does not support life so well as does ordinary water.

Q. 31. What is the difference between the terms 'hydrolysis' and 'hydration' ?

Ans. Hydrolysis is the interaction of H^+ and OH^- ions of water with the anion and cation of a salt respectively to form acid and base. For example,

$$\underset{\text{Salt}}{Na_2CO_3(s)} + 2H_2O \longrightarrow \underset{\text{Base}}{2NaOH} + \underset{\text{Acid}}{H_2CO_3}$$

Hydraton is the interaction of water with the salts to forms coordinated or hydrated ions or hydrated salts.

$$Na^+Cl^-(s) + nH_2O \longrightarrow Na^+(H_2O)_x + Cl^-(H_2O)_x$$
$$Ni^+ + 6H_2O(l) \longrightarrow Ni(H_2O)_6\ (aq)$$
$$CuSO_4(s) + 5H_2O(l) \longrightarrow \underset{\text{Hydrated salt}}{CuSO_4(s).\ 5H_2O}$$

Q. 32. How can saline hydrides remove traces of water from organic compounds ?

Ans. Saline hydrides (*e.g.*, NaH, CaH_2, etc) react with water forming their corresponding metal hydroxides with the liberation of H_2 gas. Thus, traces of water present in organic solvents can be easily removed by distilling them over saline hydrides when H_2 gas escapes into the atmosphere and metal hydroxide is left in the flask while dry organic solvent distils over.

Q. 33. What do you expect the nature of hydrides is, if formed by elements of atomic numbers 15, 19, 23 and 44 with dihydrogen ? Compare their behaviour towards water.

Ans. (*i*) Element with Z = 15 is a non-metal (*i.e.,* P) and hence form covalent hydride (PH_3).

(*ii*) Element with Z = 19 is an alkali metal (K) and hence form ionic or saline hydride (K^+H^-).

(*iii*) Element with Z = 23 is a transition element (*i.e.,* V) of group 5 and hence forms metallic or interstitial hydride (*i.e.,* $VH_{1.6}$).

(*iv*) Element with Z = 44 is a transition metal (Ru) of group 8 and therefore, it does not form any hydride.

Behaviour towards water. Only ionic hydrides (*e.g.*, K^+H^-) react with water evolving H_2 gas as

$$2KH\ (s) + \underset{\text{Water}}{2H_2O(l)} \longrightarrow 2KOH\ (aq) + 2H_2\ (l)$$

Q. 34. Do you expect different products in solution when aluminium (III) chloride and potassium chloride treated separately with (i) normal water (ii) acidified water, and (iii) alkaline water ? Write equations wherever necessary.

Ans. $AlCl_3$ is a salt of a weak base Al $(OH)_3$ and a strong acid HCl. Therefore, in normal water, it undergoes hydrolysis as :

$$AlCl_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3H^+(aq) + 3Cl^-(aq)$$

In acidic water, H^+ ions react with $Al(OH)_3$ to form $Al^{3+}(aq)$ ions and water. Thus, in acidic water $AlCl_3$ exists as $Al^{3+}(aq)$ and $Cl^-(aq)$ ions.

$$AlCl_3(s) \xrightarrow[\text{water}]{\text{acidified}} Al^{3+}(aq) + 3Cl^-(aq)$$

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In alkaline water, $Al(OH)_3$ reacts to form tetra hydroxoaluminate complex or metaluminate ion :

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow \underset{\text{Tetrahydroxo aluminate ion}}{[Al(OH)_4]^-} \text{ or } \underset{\text{Metaaluminate ion}}{AlO_2^-} + 2H_2O(l)$$

The complete reaction may be written as :

$$AlCl_3(s) \xrightarrow[\text{water}]{\text{alkaline}} [Al(OH)_4]^-(aq) + 3Cl(aq)$$
$$\downarrow OH^-$$
$$AlO_2^- + 2H_2O(l) + 3Cl^-(aq)$$

Potassium chloride is a salt of a strong acid and a strong base. It does not undergo hydrolysis in normal water. It dissociates to $K^+(aq)$ and $Cl^-(aq)$ ions as:

$$KCl(s) \xrightarrow{\text{Water}} K^+(aq) + Cl^-(aq)$$

Therefore, the aqueous solution of KCl is neutral and hence the ions donot react in acidified or alkaline water.

Q. 35. How does H_2O_2 behave as a bleaching agent ?

Ans. Hydrogen peroxide acts as a bleaching agent due to the release of nascent oxygen :

$$H_2O_2 \longrightarrow H_2O + O$$

The nascent oxygen combines with colouring matter which in turn gets oxidised. Thus, the bleaching action of H_2O_2 is due to the oxidation of colouring matter by nascent oxygen. It is used for bleaching materials like ivory, silk, wool, feathers, etc.

Q. 36. What do you understand by the terms :

(*i*) hydrogen economy, (*ii*) hydrogenation, (*iii*) syn gas, (*iv*) water-gas shift reaction (*v*) fuel cell.

Ans. (*i*) *Refer Text Page 31.*

(*ii*) *Refer Text* Chemical properties of H_2; Property 5(*ii*); Page 7.

(*iii*) *Refer Text* Commercial preparation of hydrogen; Page 6.

(*iv*) *Refer Text* Commercial preparation of pure hydrogen; Page 6.

(*v*) Fuel cell : It is a device which converts the energy produced during the combustion of a fuel directly into electrical energy. Dihydrogen is used in hydrogen-oxygen fuel cell for generating electrical energy. It has many advantages over conventional fossil fuels and electric power. It does not produce any pollution and releases larger energy per unit mass of fuel in comparison to gasoline and other fuels.

NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 54.*

Short Answer Questions *Carrying 2 or 3 marks*

Q.1. How can production of hydrogen from water gas be increased by using water gas shift reaction ?

Ans. Water gas is produced when superheated steam is passed over red hot coke or coal at 1270 K in the presence of nickel as catalyst.

$$\underset{\text{Steam}}{C(s) + H_2O(g)} \longrightarrow \underbrace{CO(g) + H_2(g)}_{\text{Water gas}} - 121.3 \text{ kJ}$$

Pure H_2 from water gas cannot be obtained easily because it is difficult to remove CO. Therefore, to increase the production of H_2 from water gas, CO is oxidised to CO_2 by mixing it with more steam and passing the mixture over heated $FeCrO_4$ catalyst at 673 K.

$$\underbrace{H_2 + CO}_{\text{Water gas}} + H_2O \xrightarrow[FeCrO_4]{673\text{ K}} CO_2 + 2H_2$$

The CO_2 produced is removed by scrubbing with sodium arsenite solution.

Q.2. What are metallic/interstitial hydrides ? How do they differ from molecular hydrides ?

Ans. *Refer Text; Page 13 and 11.*

Q.3. Name the classes of hydrides to which H_2O, B_2H_6 and NaH belong.

Ans. H_2O : Covalent or molecular hydride

B_2H_6 : Electron deficient molecular hydride

NaH : ionic hydride

Q.4. If same mass of liquid water and a piece of ice is taken, then why is the density of ice less than that of liquid water ?

Ans. Since water expands on freezing, therefore, volume of ice for the same mass of water is more than liquid water. Hence mass per unit volume *i.e.*, density of ice is lower than liquid water.

Q.5. Complete the following equations :

(*a*) $PbS(s) + H_2O_2(aq) \longrightarrow$

(*b*) $CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{Cobalt}}$

Ans. (*a*) $PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$

(*b*) $CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{Cobalt}} \underset{\text{Methanol}}{CH_3OH(l)}$

Q.6. Give reasons :

(*i*) Lakes freeze from top towards bottom.

(*ii*) Ice floats on water.

Ans. (*i*) *Refer HOTS, Q.13 (Page 44).*

(*ii*) *Refer Q.4.*

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Q.7. What do you understand by the term 'auto protolysis of water ? What is its significance ?

Ans. *Refer NCERT Qs. Q.18.*

Q.8. Discuss briefly de-mineralisation of water by ion exchange resin.

Ans. *Refer Text; Page 21.*

Q.9. Molecular hydrides are classified as electron deficient, electron precise and electron rich compounds. Explain each type with two examples.

Ans. *Refer Text; Page 11–12.*

Q.10. How is heavy water prepared ? Compare its physical properties with those of ordinary water.

Ans. *Refer Text; Page 19–20.*

Q.11. Write one chemical reaction for the preparation of D_2O_2.

Ans. D_2O_2 can be prepared by the reaction of D_2SO_4 dissolved in water over BaO_2.

$$BaO_2 + D_2SO_4 \longrightarrow BaSO_4 + D_2O_2$$

Q.12. Calculate the strength of 5 volume H_2O_2 solution.

Ans. 5 volume H_2O_2 solution means that 1 L of 5 volume H_2O_2 on decomposition gives 5L of O_2 at NTP.

$$H_2O_2 \longrightarrow 2H_2O + O_2$$

68 g 22.4 L at NTP

22.4 L of O_2 at NTP is produced from H_2O_2 = 68 g

5 L of O_2 at NTP is produced from $H_2O_2 = \frac{68}{22.4} \times 5$

$= 15.18$ g

But 5L of O_2 at NTP is produced from 1 L of 5 volume H_2O_2

Strength of H_2O_2 in 5 volume H_2O_2 = 15.18 g/L

Percentage strength of H_2O_2 solution $= \frac{15.18}{1000} \times 100$

$= 1.518\ \%$

Q.13. (*i*) Draw the gas phase and solid phase structure of H_2O_2.

(*ii*) H_2O_2 is a better oxidising agent than water. Explain.

Ans. (*i*) *Refer Fig. 9; Page 28.*

(*ii*) H_2O_2 is better oxidising agent than water because

(*a*) it oxidises an acidified KI solution to I_2 which gives blue colour with starch solution but water does not.

(*b*) H_2O_2 turns black PbS to white $PbSO_4$ but water does not.

Q.14. Melting point, enthalpy of vapourisation and viscosity data of H_2O and D_2O is given below :

	H_2O	D_2O
Melting point / K	**373.0**	**374.4**
Enthalpy of vapourisation at (373 K)/kJ mol^{-1}	**40.66**	**41.61**
Viscosity / centipoise	**0.8903**	**1.107**

On the basis of this data explain in which of these liquids intermolecular forces are stronger ?

Ans. Intermolecular forces of attraction are stronger in D_2O than in water.

Q.15. Dihydrogen reacts with dioxygen (O_2) to form water. Write the name and formula of the product when the isotope of hydrogen which has one proton and one neutron in its nucleus is treated with oxygen ? Will the reactivity of both the isotopes be the same towards oxygen ? Justify your answer.

Ans. The isotope of hydrogen containing one proton and one neutron is deuterium (D).

$$2D_2(g) + O_2(g) \longrightarrow 2D_2O$$

Deuterium oxide

Since D – D bond is stronger than H – H bond, therefore, D_2 is less reactive towards oxygen than H_2.

Q.16. Explain why HCl is a gas and HF is a liquid.

Ans. *Refer text.* (because of hydrogen bonding).

Q.17. When the first element of the periodic table is treated with dioxygen, it gives a compound whose solid state floats on its liquid state. This compound has an ability to act as an acid as well as a base. What products will be formed when this compound undergoes auto ionisation ?

Ans. The first element is hydrogen and its molecular form is dihydrogen (H_2). It reacts with oxygen to form water whose solid state is ice which is lighter than water and floats over water.

Water is amphoteric in nature *i.e.*, it acts as an acid in the presence of strong bases and acts as a base in the presence of strong acids.

As an acid

$$H_2O(l) + NH_3(aq) \longrightarrow NH_4^+(aq) + OH^-(aq)$$

acid base

As a base

$$H_2O\ (l) + H_2S\ (aq) \longrightarrow H_3O^+ + HS^-$$

base acid

Due to amphoteric nature, water undergoes self ionization as

$$H_2O + H_2O \longrightarrow H_3O^+ + OH^-$$

Q.18. Rohan heard that instructions were given to the laboratory attendent to store a particular chemical i.e., keep it in the dark room, add some urea in it, and keep it away from dust. This chemical acts as an oxidising as well as a

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reducing agent in both acidic and alkaline media. This chemical is important for use in the pollution control treatment of domestic and industrial effluents.

(*i*) Write the name of this compound.

(*ii*) Explain why such precautions are taken for storing this chemical.

Ans. (*i*) Hydrogen peroxide, H_2O_2.

(*ii*) H_2O_2 decomposes in the presence of light and dust particles. Therefore, it is stored in wax-lined glass or plastic vessels in the presence of stabilizers like urea. It is also kept away from dust.

Q.19. Give reasons why hydrogen resembles alkali metals ?

Ans. *Refer Text; Page 1.*

Q.20. Hydrogen generally forms covalent compounds. Give reason.

Ans. *Refer Text; Page 2.*

Q.21. Why is the ionisation enthalpy of hydrogen higher than that of sodium ?

Ans. The size of hydrogen is smaller than that of sodium and therefore, the ionization enthalpy of H is higher (1312 kJ mol^{-1}) than that of Na (496 kJ mol^{-1}).

Q.22. Basic principle of hydrogen economy is transportation and storage of energy in the form of liquid or gaseous hydrogen. Which property of hydrogen may be useful for this purpose ? Support your answer with the chemical equation if required.

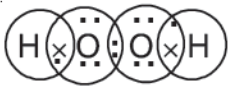
Ans. Basic property of hydrogen economy is that it can be converted into liquid by cooling under high pressure and therefore, can be easily transported, *Refer Text; Page 993.*

Q.23. What is the importance of heavy water ?

Ans. *Refer Text; Page 19.*

Q.24. Write the Lewis structure of hydrogen peroxide.

Ans.



Q.25. An acidic solution of hydrogen peroxide behaves as an oxidising as well as reducing agent. Illustrate it with the help of a chemical equation.

Ans. *Refer Text page 25.*

Q.26. With the help of suitable examples, explain the property of H_2O_2 that is responsible for its bleaching action ?

Ans. *Refer Text; Page 27.*

Q.27. Why is water molecule polar ?

Ans. Due to difference in electronegativity between O and H and angular shape. *Refer Text; Page 16.*

Q.28. Why does water show high boiling point as compared to hydrogen sulphide ? Give reasons for your answer.

Ans. Due to hydrogen bonding. *Refer Text; Page 16.*

Q.29. Why can dilute solutions of hydogen peroxide not be concentrated by heating. How can a concentrated solution of hydrogen peroxide be obtained ?

Ans. H_2O_2 cannot be concentrated simply by heating because it decomposes much below its boiling point. Therefore, concentration of H_2O_2 is carried out in a number of stages. *Refer Text; Page 24.*

Q.30. Why is hydrogen peroxide stored in wax-lined bottles ?

Ans. Hydrogen peroxide is decomposed by the rough surfaces of glass, alkali oxides present in it and light. Therefore, to prevent its decomposition, H_2O_2 is usually stored in coloured paraffin wax coated plastic or teflon bottles.

Q.31. Why does hard water not form lather with soap ?

Ans. *Refer Text; Page 20.*

Q.32. Phosphoric acid is preferred over sulphuric acid in preparing hydrogen peroxide from peroxides. Why ?

Ans. H_2SO_4 acts as a catalyst for decomposition of H_2O_2. Therefore, some weaker acid such as H_3PO_4 is preferred over H_2SO_4 for preparing H_2O_2 from peroxides

$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O_2$$

Q.33. How will you account for 104.5° bond angle in water ?

Ans. *Refer Text* (because of presence of 2 lone pairs); Page 15–16.

Q.34. Write redox reaction between fluorine and water.

Ans. $2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2$

Q.35. Write two reactions to explain amphoteric nature of water.

Ans. *Refer Text; Page 17 and Q. 17.*

Long Answer Questions *Carrying 5 marks*

Q.36. Atomic hydrogen combines with almost all elements but molecular hydrogen does not. Explain.

Ans. Atomic hydrogen is highly unstable and hence very reactive. Therefore, it combines with almost all the elements. However, molecular hydrogen has large bond dissociation enthalpy (458.5 kJ mol^{-1}) and therefore, less reactive.

Q.37. How can D_2O be prepared from water ? Mention the physical properties in which D_2O differs from H_2O. Give at least three reactions of D_2O showing the exchange of hydrogen with deuterium.

Ans. *Refer Text; Page 19.*

Q.38. How will you concentrate H_2O_2 ? Show differences between structures of H_2O_2 and H_2O by drawing their spatial structures. Also mention three important uses of H_2O_2.

Ans. *Refer Text; Page 24, 27-28.*

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Q.39. (*i*) Give a method for the manufacture of hydrogen peroxide and explain the reactions involved therein.

(*ii*) Illustrate oxidising, reducing and acidic properties of hydrogen peroxide with equations.

Ans. *Refer Text; Page 23, 24,25.*

Q.40. What mass of hydrogen peroxide will be present in 2 litres of a 5 molar solution ? Calculate the mass of oxygen which will be liberated by the decomposition of 200 mL of this solution.

Ans. Molar mass of H_2O_2 = 34 g mol^{-1}

1L of 5M solution of H_2O_2 will contain H_2O_2
= 34 × 5g

2L of 5M solution of H_2O_2 will contain H_2O_2
= 2 × 34 × 5 = 340 g

200 mL of 5M solution will contain H_2O_2

$$= \frac{340}{2000} \times 200 = 34 \text{ g}$$

$$2H_2O_2 \longrightarrow H_2O + O_2$$

68 g of H_2O_2 on decomposition will give O_2 = 32 g

∴ 34 g of H_2O_2 on decomposition will give O_2

$$= \frac{32}{68} \times 34 = \mathbf{16\ g}.$$

Q.41. A colourless liquid 'A' contains H and O elements only. It decomposes slowly on exposure to light. It is stabilised by mixing urea to store in the presence of light.

(*i*) Suggest possible structure of A.

(*ii*) Write chemical equations for its decomposition reaction in light.

Ans. The liquid A is hydrogen peroxide (H_2O_2).

(*i*) For structure *Refer Fig.* 9; *Page 28.*

(*ii*) $2H_2O_2 \xrightarrow{\text{Light}} 2H_2O + O_2$

Q.42. An ionic hydride of an alkali metal has significant covalent character and is almost unreactive towards oxygen and chlorine. This is used in the synthesis of other useful hydrides. Write the formula of this hydride. Write its reaction with Al_2Cl_6.

Ans. Since the ionic hydride of alkali metal has significant covalent character, therefore, it is LiH. Since LiH is very stable, therefore, it is almost unreactive towards O_2 and Cl_2.

It reacts with Al_2Cl_6 to form lithium aluminium hydride

$$8LiH + Al_2Cl_6 \longrightarrow 2LiAlH_4 + 6LiCl$$

Q.43. Sodium forms a crystalline ionic solid with dihydrogen. The solid is non-volatile and non-conducting in nature. It reacts violently with water to produce dihydrogen gas. Write the formula of this compound and its reaction with water. What will happen on electrolysis of the melt of this solid?

Ans. Sodium reacts with dihydrogen to form sodium hydride which is a crystalline ionic solid.

$$2Na + H_2 \longrightarrow 2NaH \text{ or } 2Na^+H^-$$

It reacts with water to produce H_2 gas.

$$2NaH + 2H_2O \longrightarrow 2NaOH + H_2(g)$$

Although Na^+H^- does not conduct electricity in the solid state, but electrolysis of its melt give H_2 gas at anode and Na at cathode.

$$2Na^+H^- \xrightarrow{\text{Electrolysis}} \underset{\text{At cathode}}{2Na(l)} + \underset{\text{At anode}}{H_2(g)}$$

QUICK MEMORY TEST

A. Say True or False

1. Decomposition of hydrogen peroxide is an exothermic reaction.
2. Electrolysis of HCl(*aq*) gives hydrogen at cathode.
3. Syngas is a mixture of H_2 and CO_2.
4. Dihydrogen reacts with CO at 700K in the presence of a catalyst ZnO/Cr_2O_3 to form formaldehyde.
5. Magnesium boride reacts with water to give boric acid.
6. Water has maximum density at 277K.
7. Heavy water was discovered by Urey.
8. The bleaching action of H_2O_2 is permanent and is due to oxidation.
9. The permanent hardness of water is due to chlorides and sulphates of calcium and magnesium.
10. Calgon is $Na_2[Na_4(PO_4)_3]$.

B. Complete the missing links

1. The electrolysis of molten sodium hydride liberates hydrogen gas at .....
2. Heavy water was discovered by .....
3. The hardness due to the presence of chlorides and sulphates of calcium and magnesium dissolved in it is called ..... hardness.
4. Heavy water is used as ..... in nuclear reactors.
5. Hydrogen peroxide oxidises hydrogen sulphide to .....
6. 11.2 L of O_2 at N.T.P. is produced from ..... g of H_2O_2.
7. Among HF, NH_3 and H_2O, maximum hydrogen bonding occurs in .....
8. The isotope of hydrogen commonly used as a tracer in organic reactions is .....
9. Bleaching action of H_2O_2 is due to its ..... nature.
10. Hydrogen gas is liberated by the action of aluminium with concentrated solution of .....

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C. Choose the correct alternative

1. Most of the *d*- and *f*-block elements form *metallic/covalent* hydrides.
2. Methane is an *electron precise/electron rich* molecular hydride.
3. At 0K, hydrogen contains mainly *para/ortho* hydrogen.
4. The hardness in water due to the presence of bicarbonates of calcium is called *permanent/temporary* hardness.
5. Calcium and magnesium ions in water combine with Calgon to form *soluble/insoluble* complex ions.
6. *MnO_2/acetanilide* checks the decomposition of H_2O_2.
7. The bleaching action of H_2O_2 is due to *reduction/oxidation*.
8. Viscosity of D_2O is *more/less* than H_2O.
9. Electron deficient molecular hydride is *B_2H_6/NH_3*.
10. Molecules of hydrogen in which the spins of both the nuclei are in the same direction is called *ortho/para* hydrogen.

Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. True
3. **False :** Syngas is a mixture of H_2 and CO.
4. **False :** It forms methanol.
5. **False :** It forms diborane.
6. True
7. True
8. True
9. True
10. **False :** Calgon is $Na_2[Na_4(PO_3)_6]$.

B. Complete the missing links

1. anode
2. Urey
3. permanent
4. moderator
5. sulphur
6. 34
7. HF
8. deuterium
9. oxidising
10. sodium hydroxide

C. Choose the correct alternative

1. metallic
2. electron precise
3. para
4. temporary
5. soluble
6. acetanilide
7. oxidation
8. more
9. B_2H_6
10. ortho.

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Why is hydrated barium peroxide used in the preparation of hydrogen peroxide instead of anhydrous barium peroxide ?

Ans. If anhydrous barium peroxide is used in the preparation of H_2O_2, the barium sulphate formed during the reaction forms an insoluble protective coating on the surface of solid barium peroxide.

$$BaO_2(s) + H_2SO_4(aq) \longrightarrow \underset{\text{Insoluble}}{BaSO_4(s)} + H_2O_2(aq)$$

This prevents further action of acid and therefore, stops the reaction. If, however, hydrated barium peroxide (in the form of thin paste) is used, the water of crystallisation does not allow $BaSO_4$ to deposit on the surface of BaO_2 and the reaction goes to completion.

Q.2.Hydrogen is not prepared by the reaction of concentrated sulphuric acid on zinc. Explain.

Ans. Concentrated sulphuric acid is not used for the preparation of hydrogen because it reacts with zinc to form SO_2 gas instead of hydrogen.

$$Zn + 2H_2SO_4(\text{conc.}) \longrightarrow ZnSO_4 + SO_2 + 2H_2O$$

Q. 3.Which element can oxidise water to O_2? Justify.

Ans. Fluorine being more electronegative than oxygen can oxidise water to oxygen. In this, water acts a reducing agent and hence itself gets oxidised to O_2.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

Q.4. Dilute solution of hydrogen peroxide cannot be heated strongly for its concentration. Explain.

Ans. Dilute solution of H_2O_2 cannot be concentrated by heating because it decomposes into H_2 and O_2 on heating.

$$H_2O_2 \xrightarrow{\text{heat}} H_2 + O_2$$

Q.5. Can sodium bicarbonate make water hard ? Explain.

Ans. Sodium bicarbonate cannot make water hard because soaps themselves are sodium salts of fatty acids which are soluble in water.

Q.6. Why is phosphoric acid preferred to sulphuric acid in the preparation of H_2O_2 from barium peroxide? Explain.

Ans. The aqueous solution of H_2O_2 prepared by the action of dil. H_2SO_4 on hydrated BaO_2 contains impurities

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of heavy metal ions such as Ba^{2+}, Pb^{2+}, etc. These catalyse the decomposition of H_2O_2 and therefore, the solution cannot be stored for a long time. To prevent this, phosphoric acid is preferred to sulphuric acid because impurities of heavy metal ions get completely precipitated as insoluble phosphates and the solution does not contain any free heavy metal ions to catalyse the decomposition of H_2O_2. Therefore, it can be safely stored for a longer time.

Q.7.Statues coated with white lead on long exposure to atmosphere turn black and their original colour can be restored on treatment with H_2O_2. Why ?

Ans. On long exposure to atmosphere, white lead gets converted to black PbS due to action of H_2S present in the atmosphere.

$$\underset{}{PbO_2} + \underset{\text{from atmosphere}}{H_2S} \longrightarrow \underset{\text{Black}}{PbS} + 2H_2O$$

As a result, statues turn black. On treatment of these black statues with H_2O_2, the black PbS gets oxidised to $PbSO_4$ and their colour is restored.

$$PbS + H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

Q.8. Which of the two : hydrogen or deuterium undergoes reactions more rapidly and why ?

Ans. Hydrogen undergoes reactions more rapidly than deuterium. This is because of mass differences. For example, reaction between hydrogen and chlorine is about 14 times faster than between deuterium and chlorine.

Q. 9. Why can't sea animals live in distilled water ?

Ans. Distilled water does not contain dissolved O_2. Therefore, sea animals cannot live in distilled water because of the absence of dissolved oxygen for breathing.

Q.10. Concentrated sulphuric acid cannot be used for drying H_2. Why ?

Ans. Conc. H_2SO_4 on absorbing water from moist H_2 produces so much heat that H_2 catches fire.

Q.11. Can we remove completely temporary hardness due to $Mg(HCO_3)_2$ by boiling ?

Ans. Temporary hardness of water due to $Mg(HCO_3)_2$ can be completely removed by boiling because soluble $Mg(HCO_3)_2$ is converted into insoluble $MgCO_3$ which can be easily removed by filtration.

$$\underset{\text{Soluble}}{Mg(HCO_3)_2} \xrightarrow{\text{Boil}} \underset{\text{Insoluble}}{MgCO_3} + CO_2 + H_2O$$

Q.12. H_2O_2 acts as an oxidising agent as well as reducing agent. Why ?

Ans. In H_2O_2, oxygen has -1 oxidation state which lies between maximum (0 or +2 in OF_2) and minimum –2. Therefore, oxygen can be oxidised to O_2 (zero oxidation state) acting as reducing agent or can be reduced to H_2O or OH^- (–2 oxidation state) acting as an oxidising agent.

$$\underset{}{\overset{-1}{O_2}} \longrightarrow \overset{0}{O_2} + 2e^-$$

Reducing agent

$$\overset{-1}{O_2} + 2e^- \longrightarrow \overset{2-}{2O}$$

Oxidising agent

Q.13. Why do lakes freeze from top towards bottom ?

Ans. The density of ice is less than that of liquid water. Therefore, ice floats on the surface. Thus, the ice layer at lower temperature floats over the water below it. Due to this the freezing of water into ice occurs continuously from top towards bottom.

Q.14. A mixture of H_2O_2 and hydrazine with copper (II) is used as a rocket propellant. Why ?

Ans. The reaction between hydrazine and H_2O_2 in the presence of Cu(II) is highly exothermic and is accompanied by a large increase in volume of the products. Therefore, this mixture is used as a rocket propellant.

$$\underset{\text{Hydrazine}}{2H_2O_2(l) + H_2NNH_2(l)} \xrightarrow{Cu(II)} N_2(g)\uparrow + 4H_2O(g)\uparrow$$

Q.15. Water cannot be used to extinguish petrol fires. Why ?

Ans. Water is used to extinguish most fires because it lowers the temperature of burning material. However, in case of petrol fires, petrol being lighter than water, floats over water and hence fire spreads instead of being extinguished.

Q.16. Ferric chloride is reduced when zinc and hydrochloric acid are added to its solution and not by passing H_2 gas through its solution. Explain

Ans. Ordinary H_2 is less reactive and therefore, it does not reduce acidified $FeCl_3$ solution. However, when zinc is added to acidified $FeCl_3$ solution, nascent hydrogen is produced which has enormous energy. It is more reactive than ordinary H_2 and reduces acidified $FeCl_3$ solution.

$$FeCl_3 + H_2 \longrightarrow \text{No reaction}$$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + \underset{\text{nascent hydrogen}}{H_2^*}$$

$$2FeCl_3 + H_2^* \longrightarrow \underset{\text{Green}}{2FeCl_3} + 2HCl$$

Q.17. Hard water is softened before using in boilers. Explain.

Ans. Hard water on boiling forms precipitates of $MgCO_3$, $CaCO_3$ and $CaSO_4$ which form scales in the boilers. As of result of these scales in the boilers, the boiler gets deteriorated due to over heating. Moreover, these scales are non-conducting and therefore, more fuel is consumed. Therefore, in order to prevent the formation of scales, hard water is softened before using in boilers.

Q.18. Why is hydrogen peroxide stored in wax-lined plastic coloured bottles ?

Ans. The decomposition of H_2O_2 occurs readily in the presence of rough surface (acting as catalyst). It is also decomposed by exposure of light. Therefore, wax-lined smooth surface and coloured bottles retard the decomposition of H_2O_2.

Q.19. Presence of water is avoided during the preparation of H_2O_2 from Na_2O_2. Why ?

Ans. Water present during the reaction, reacts with Na_2O_2 to form NaOH which tends to decompose H_2O_2.

$$Na_2O_2 + 2H_2O \longrightarrow H_2O_2 + 2NaOH$$

$$2H_2O_2 \xrightarrow{NaOH} 2H_2O + O_2$$

Q.20. An aqueous solution of an inorganic compound (X) shows the following reactions :

***(i)* It decolourises an acidified $KMnO_4$ solution accompanied with evolution of oxygen gas.**

***(ii)* It liberates iodine from acidified potassium iodide solution.**

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(*iii*) It gives brown precipitate with alkaline $KMnO_4$ solution with evolution of oxygen gas.

(*iv*) It removes black stains from old oil paintings.

Identify (X) and give chemical reactions for steps (*i*) to (*iv*).

Ans. Since X removes black stains from old oil paintings, it is hydrogen peroxide H_2O_2.

(*i*) $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow$
(X) $K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

(*ii*) $H_2O_2 + 2KI + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2H_2O$

(*iii*) $3H_2O_2 + 2KMnO_4 \longrightarrow$
(X) $2\,MnO_2 + 2\,KOH + 3O_2 + 2H_2O$
Brown ppt

(*iv*) $4H_2O_2 + PbS \longrightarrow PbSO_4 + 4H_2O$
(black) white

Q.21. To a 25 mL H_2O_2 solution, excess of acidified solution of KI was added. The iodine liberated required 20.0 mL of 0.3 N $Na_2S_2O_3$ solution. Calculate the volume strength of H_2O_2 solution.

Ans. Applying normality equation,

$$\underbrace{N_1V_1}_{H_2O_2} = \underbrace{N_2\ V_2}_{Na_2S_2O_3}$$

$$N_1 \times 25 = 0.3 \times 20$$

$$\therefore \quad N_1 = \frac{0.3\times 20}{25} = 0.24\,N$$

Strength of $H_2O_2 = 0.24 \times 17 = 4.08$ g/L

$2H_2O_2 \longrightarrow 2H_2O + O_2$
$2 \times 34 = 68$ g 22400 mL

68 g of H_2O_2 produce O_2 at N.T.P. = 22400 mL

4.08 g of H_2O_2 will produce O_2 at N.T.P.

$$= \frac{22400}{68} \times 4.08 = 1344 \text{ mL}$$

Now 4.08 g of H_2O_2 are present in 1000 mL of solution.

$\therefore$ 1000 mL of H_2O_2 solution give 1344 mL of O_2 at N.T.P.

$\therefore$ 1 mL of H_2O_2 solution will give $= \frac{1344}{1000} = 1.344$ mL of O_2 at N.T.P.

$\therefore$ Volume strength of $H_2O_2 = 1.344$

Q.22. Calculate the volume of 10 volume H_2O_2 required to neutralise 200 mL of 2N $KMnO_4$ in acidic medium.

Ans. $2H_2O_2 \longrightarrow 2H_2O + O_2$
68 g 22.4 L at N.T.P.

22.4 L of O_2 at N.T.P. is produced from $H_2O_2 = 68$ g

10 L of O_2 at N.T.P. is produced from $H_2O_2 = \frac{68}{22.4} \times 10$

$= 30.357$ g

Gram equivalents of $H_2O_2 = \frac{30.357}{17} = 1.79$

Normality of $H_2O_2 = \frac{1.79}{1} = 1.79$ N

Applying normality equation,

$$\underbrace{N_1V_1}_{H_2O_2} = \underbrace{N_2\ V_2}_{KMnO_4}$$

$$(H_2O_2) \quad KMnO_4$$
$$1.79 \times V_1 = 2 \times 200$$

$$V_1 = \frac{2\times 200}{1.79} = 223.5 \text{ mL}$$

Q.23. 0.5 L each of three samples of H_2O_2 labelled 10 vol, 15 vol and 20 vol are mixed and then diluted with equal volume of water. What is the strength of resultant H_2O_2 solution ?

Ans. Volume strength of H_2O_2 solution
$= 5.6 \times$ Normality

$$\text{Normality} = \frac{\text{Vol. strength}}{5.6}$$

Normality of 10 vol of $H_2O_2 = \frac{10}{5.6}$N

Normality of 15 vol of $H_2O_2 = \frac{15}{5.6}$N

Normality of 20 vol of $H_2O_2 = \frac{20}{5.6}$N

Let 500 mL of each solution is mixed and then total volume of mixture becomes = 1500 mL. Since it is diluted with equal volume of water, total volume becomes 3000 mL.

Applying normality equation

$N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$

$$\frac{10\times 500}{5.6} + \frac{15\times 500}{5.6} + \frac{20\times 500}{5.6} = N_4 \times 3000$$

$$\therefore N_4 = \frac{45\times 500}{5.6\times 3000} = 1.339\ N$$

Volume strength of resulting solution $= 1.339 \times 5.6 = 7.5$

Q.24. The degree of hardness of a given sample of hard water is 60 ppm. If the entire hardness is due to $MgSO_4$, how much of $MgSO_4$ is present per kilogram of hard water ?

Ans. Degree of hardness of water = 60 ppm

Since degree of hardness is the number of parts of calcium carbonate or equivalent to calcium and magnesium salts present in a million parts of water by mass,

$\therefore$ 10^6 g of water contain 60 g of $CaCO_3$.

Now 1 mol of $CaCO_3$ = 1 mol of $MgSO_4$

100 g of $CaCO_3$ = 120 g of $MgSO_4$

$$10^6 \text{ g of water contain } MgSO_4 = \frac{60\times 120}{100} = 72 \text{ g}$$

$$10^3 \text{ g of water will contain } MgSO_4 = \frac{72}{10^6} \times 10^3 = 0.072 \text{ g}$$

$\therefore$ 1 kg of water contains $MgSO_4 = 72$ mg

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Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Name the three isotopes of hydrogen.
2. What is meant by 10 volume hydrogen peroxide ?
3. Name the element which when treated with dilute H_2SO_4 gives pure hydrogen.
4. Give a compound in which hydrogen exists in the negative oxidation state.
5. Give two advantages of using hydrogen as fuel over gasoline.
6. Explain why H_2O_2 cannot be stored for prolonged periods?
7. Why does H_2O have a higher melting and boiling points as compared to H_2S ?
8. What is heavy water ? What is the mass of 1 mole of heavy water ?
9. Name two metals which can displace hydrogen from acids.
10. Which isotope of hydrogen is radioactive in nature ?
11. Can sodium bicarbonate make water hard ?
12. What is meant by autoprotolysis of water ?
13. Which of the two Cl_2 or Br_2 more reactive towards dihydrogen?
14. How does H_2O_2 react with lead dioxide ?
15. The bleaching action of H_2O_2 is due to oxidation or reduction?
16. What happens when peroxydisulphuric acid is hydolysed with water ?
17. Give an example each of ionic hydride and covalent hydride.
18. Name the gases produced when water reacts with :
    (*i*) Aluminium nitride (*ii*) Aluminium carbide.
19. Complete the reaction :
    $SiCl_4 + H_2O \longrightarrow$
20. Complete the reaction :
    $PbS + H_2O_2 \longrightarrow$
21. Complete the following reactions :
    $CaO\ (s) + H_2O\ (l) \longrightarrow$
    $Na_2O\ (s) + H_2O\ (l) \longrightarrow$
22. Why do lakes freeze from top towards bottom ?
23. Explain why water has higher melting and boiling points than H_2S.
24. Account for the amphoteric character of water.
25. What is meant by hydrogenation ?
26. How is temporary hardness in water removed?
27. Which cations cause hardness in water?
28. Which anions cause hardness in water?

Short Answer Questions *Carrying 2 or 3 marks*

1. How is H_2O_2 manufactured by the electrolysis of water ? Give its structure.
2. What are the ways in which the water molecules bonded to anhydrous salt to form a hydrate ?
3. Name the class of hydrides to which NaH, H_2O_2, B_2H_6 and LaH_3 belong. What is understood by hydride gap ?
4. Compare the structural properties of H_2O and H_2O_2.
5. What causes the temporary and permanent hardness of water ?
6. Explain why hydrogen is best placed separately in the periodic table of elements.
7. Discuss the principle and method of softening of hard water by synthetic ion exchange resins.
8. Discuss the structure of common form of ice.
9. Show how can hydrogen peroxide function both as an oxidising and reducing agent.
10. Complete the following reactions :
    (*i*) $AlN + H_2O \longrightarrow$ (*ii*) $CaC_2 + H_2O \longrightarrow$
11. How does H_2O_2 react with (*i*) potassium ferricyanide (*ii*) lead sulphide ?
12. What is the structure of hydrogen peroxide ? Give its four uses.
13. Why is anhydrous barium peroxide not used in the preparation of H_2O_2? How does hydrogen peroxide react with :
    (*i*) chlorine (*ii*) moist silver oxide
    (*iii*) sodium carbonate ?
14. How is hydrogen peroxide manufactured ?
    Explain why H_2O_2 cannot be stored for long periods ?
15. Complete the following reactions :
    (*a*) $Cl_2O_7 + H_2O \longrightarrow$
    (*b*) $Sn + NaOH + H_2O \longrightarrow$
16. Compare the structures of H_2O and H_2O_2.
17. What are metallic or interstital hydrides ? How do they differ from molecular hydrides ?
18. Describe some unusual properties of water.
19. How is heavy water prepared from normal water ? Describe.
20. Write chemical reactions to show the amphoteric nature of water.
21. Hydrogen forms three types of bonds in their compounds. Describe each type of bonding using suitable examples.
22. Explain the following :
    (*a*) A solution of H_2O_2 cannot be stored for a long period.
    (*b*) Anhydrous BaO_2 cannot be used to prepare H_2O_2 by reacting with acid.
    (*c*) Liquid hydrogen cannot be used easily as a fuel.

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23. Explain
(*a*) Use of liquid hydrogen as a fuel.
(*b*) Uses of H_2O_2.

24. What is heavy water ? How does it react with :
(*i*) sodium metal (*ii*) Na_2O (*iii*) CaC_2

25. How is hydrogen prepared commercially ? Give brief account of isotope of hydrogen.

26. Give four uses of dihydrogen.

27. What happens when H_2O_2 is treated with :
(*i*) acidified potassium iodide.
(*ii*) lead sulphide.
(*iii*) alkaline solution of potassium ferrocyanide ?

28. Give structure and four uses of hydrogen peroxide.

29. Give equations for the preparation of dihydrogen
(*i*) from water using reducing agent.
(*ii*) by Lane's process.

30. What is the differences between hydrolysis and hydration ?

31. Describe the importance of heavy water in nuclear reactors.

32. Explain
(*i*) Ionic hydrides are commonly used to remove traces of water from organic compounds.
(*ii*) D_2O resembles H_2O chemically yet it is toxic substance.

33. What are covalent and ionic hydrides ? Give one example of each.

34. Explain briefly the laboratory preparation for pure hydrogen.

35. What are interstitial hydrides ? Give examples.

36. Give the preparation and two uses of $LiAlH_4$.

37. What are saline hydrides ? Give examples.

38. What are polymeric hydrides ? Give the preparation and structure of beryllium hydride.

39. What is heavy water ? Give its important uses.

40. Discuss the structure of common form of ice. Why does ice float over water ?

41. Is it correct to say that hydrogen can behave as a metal ? State the conditions under which such behaviour is possible.

42. Elements with atomic numbers 17 and 20 form compounds with hydrogen. Write the formulae of these two compounds and compare their chemical behaviour.

43. Write the formulae of the compounds of hydrogen with elements having atomic numbers 9, 11, 12 and 17. Compare their chemical behaviour.

44. Explain :
(*i*) Why water has higher boiling and melting points as compared to H_2S ?
(*ii*) Why do lakes freeze from top towards bottom ?

45. Name the isotopes of hydrogen. What is the importance of heavier isotopes of hydrogen ?

46. Name the class of hydrides which H_2O, B_2H_6, NaH, and LaH_3 belongs. What is understood by hydride gap?

47. Although D_2O resembles H_2O chemically yet it is a toxic substance. Explain.

48. What are the advantages of using hydrogen as a fuel?

49. Ionic hydrides are frequently used to remove traces of water from organic compounds. What is the underlying basis of this process ?

50. What is meant by demineralized water and how can it be obtained?

51. What is the difference between hydrolysis and hydration?

52. Write chemical reaction to justify that hydrogen peroxide can function as an oxidising as well as reducing agent?

53. How does H_2O_2 behave as a bleaching agent ?

Long Answer Questions *Carrying 5 marks*

1. Discuss the position of hydrogen in the periodic table.

2. Describe the industrial uses of hydrogen which depend upon :
(*i*) the heat liberated when it burns.
(*ii*) the ability to react with vegetable oil in the presence of a catalyst.
(*iii*) its ability to unite with nitrogen.

3. (*i*) How would you prepare dihydrogen from water using a reducing agent ?
(*ii*) How would you prepare dihydrogen from a substance other than water ?
(*iii*) How would you prepare pure dihydrogen in the laboratory ?

4. What is the mass of H_2O_2 present in 1 litre of a 2M solution ? Calculate the volume of oxygen at S.T.P. liberated upon the complete decomposition of 100 cm^3 of the above solution.

5. When hydrogen is passed over a black solid compound A, the products are grey metal B and a colourless liquid C. The metal B displaces copper from copper sulphate solution and reacts with dilute hydrochloric acid to give hydrogen.
(*i*) Name A, B and C.
(*ii*) Give the chemical equations involved.
(*iii*) How will you confirm the identity of C ?

6. How is dihydrogen prepared :
(*i*) from water by using a reducing agent.
(*ii*) in the laboratory in the pure form.
(*iii*) from hydrocarbons.

7. How is hydrogen peroxide commercially prepared by electrolysis of H_2SO_4 solution ? How is it concentrated ? Explain its oxidising and reducing character.

8. Complete the following reactions :
(*a*) $H_2S + H_2O_2 \longrightarrow$
(*b*) $H_2O_2 + 2OH^- \longrightarrow$
(*c*) $CaOCl_2 + H_2O_2 \longrightarrow$
(*d*) $C_2H_4 + H_2O_2 \longrightarrow$
(*e*) $K_2Cr_2O_7 + H_2SO_4 + H_2O_2 \longrightarrow$

9. Write short notes on.
(*a*) Concentration of hydrogen peroxide.
(*b*) Use of liquid hydrogen as fuel.
(*c*) Heavy water and its uses.

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10. Explain the following terms :
(*i*) diprotium (*ii*) dihydrogen
(*iii*) proton (*iv*) hydron.

11. Describe the industrial applications of hydrogen dependent on
(*i*) the heat liberated when its atoms combine on the surface of a metal.
(*ii*) its effect on unsaturated organic system in the presence of a catalyst.
(*iii*) its ability to combine with nitrogen under specific conditions.

12. How is hydrogen peroxides prepared ? Show by proper chemical reactions how can it function both as an oxidising and a reducing agent ? Explain its importance in nuclear reactors.

13. What do you understand by the terms :
(*i*) Hydrogen economy (*ii*) Hydrogenation
(*iii*) Syn gas (*iv*) Water-shift reaction
(*v*) Fuel cell.

Hints & Answers for Revision Exercises

Very Short Answer Questions

2. It means that 1 ml of H_2O_2 will give 10 ml of oxygen at N.T.P.

3. Magnesium **4.** NaH

8. 20 **9.** Zinc, Magnesium

10. Tritium **13.** Cl_2

14. Oxidation **17.** NaH, B_2H_6

18. (*i*) Ammonia (*ii*) Methane

27. Ca^{2+}, Mg^{2+} **28.** SO_4^{2-}, Cl^-

Short Answer Questions

10. (*i*) $AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$
(*ii*) $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

32. (*i*) H^- is a strong Bronsted base which has high reactivity with water.
(*ii*) It is because of slow rate of D^+ compared to H^+ in reactions involved in enzymatic catalysis.

42. HCl (molecular hydride), CaH_2 (ionic hydride).

43. HF, NaH, MgH_2 and HCl

Long Answer Questions

4. 68 g, 2240 cm^3

Competition File

Objective Questions

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Hydrogen

A1. The radioactive isotope of hydrogen is
(*a*) Hydrogen (*b*) Protium
(*c*) Deuterium (*d*) Tritium

A2. Which of the following metals cannot liberate hydrogen from dilute hydrochloric acid ?
(*a*) Zn (*b*) Mg
(*c*) Fe (*d*) Cu

A3. Which of the following metals give hydrogen with very dil HNO_3 ?
(*a*) Al (*b*) Mg
(*c*) Au (*d*) Sn

A4. Which of the following is most reactive towards H_2 ?
(*a*) Cl_2 (*b*) F_2
(*c*) Br_2 (*d*) I_2

A5. The least abundant isotope of hydrogen is
(*a*) ^1_1H (*b*) ^2_1D
(*c*) ^1_3T (*d*) both (*a*) and (*b*)

A6. Which of the following is not an example of ionic hydride ?
(*a*) LiH (*b*) CaH_2
(*c*) CsH (*d*) GeH_2

Answers

A1. (*d*) **A2.** (*d*) **A3.** (*b*) **A4.** (*b*) **A5.** (*c*) **A6.** (*d*)

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A7. Hydrogen combines with other elements by
(a) losing an electron
(b) gaining an electron
(c) sharing an electron
(d) losing, gaining and sharing of an electron.

A8. In which of the following pair, both the hydrides are not of the same type ?
(a) LaH_3, TiH_2 (b) CH_4, H_2S
(c) NaH, CaH_2 (d) BaH_2, SiH_4

A9. Ortho and para hydrogen differ in
(a) Atomic number
(b) Mass number
(c) Electron spin in two atoms
(d) Nuclear spin in two atoms

A10. Which of the following hydrides is electron-precise hydride ?
(a) B_2H_6 (b) NH_3
(c) H_2O (d) CH_4

A11. Hydrogen resembles halogens in many respects for which several factors are responsible. Of the following factors which one is most important in this respect ?
(a) Its tendency to lose an electron to form a cation.
(b) Its tendency to gain a single electron in its valence shell to attain stable electronic configuration.
(c) Its low negative electron gain enthalpy value.
(d) Its small size.

A12. Dihydrogen react with CO at 700K in the presence of a catalyst ZnO/Cr_2O_3 to form
(a) CH_4 (b) HCHO
(c) C_6H_6 (d) CH_3OH

Water

A13. Calcium phosphide gets hydrolysed and give
(a) $Ca_3(PO_4)_2$ (b) PH_3
(c) H_3PO_4 (d) $(HPO_3)_n$

A14. Which of the following is used as a moderator in nuclear reactors ?
(a) Hard water (b) Heavy water
(c) Deuterium (d) Deionized water

A15. One mole of calcium phosphide on reaction with excess of water gives
(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus pentoxide

A16. The salt responsible for permanent hardness of water is
(a) K_2SO_4 (b) $MgCl_2$
(c) $Mg(HCO_3)_2$ (d) NaCl

A17. Which of the following reaction is an example of use of water gas in the synthesis of other compounds ?
(a) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\ K} CO(g) + H_2(g)$
(b) $CO(g) + H_2O(g) \xrightarrow[Catalyst]{673\ K} CO_2(g) + H_2(g)$
(c) $C_nH_{2n+2} + nH_2O(g) \xrightarrow[Ni]{1270\ K} n\,CO + (2n+1)H_2$
(d) $CO(g) + 2H_2(g) \xrightarrow[Catalyst]{Cobalt} CH_3OH(l)$

A18. Which of the following compounds is used for water softening ?
(a) $Ca_3(PO_4)_2$ (b) Na_3PO_4
(c) $Na_6P_6O_{18}$ (d) Na_2HPO_4

A19. Heavy water is obtained by
(a) boiling water
(b) reacting D_2 and O_2
(c) prolonged electrolysis of H_2O
(d) heating H_2O_2.

A20. Water gas is a mixture of
(a) CO_2 and H_2O (b) CO and H_2O
(c) CO and H_2 (d) CO and N_2

Hydrogen Peroxide

A21. Hydrogen peroxide can be prepared from
(a) NaOH (b) $BaO_2.8H_2O$
(c) $Ca(OH)_2$ (d) Na_2O

A22. What is the mass of hydrogen peroxide in 1 L of 3M solution ?
(a) 10.2 g (b) 102 g
(c) 11.3 g (d) 68 g

A23. Decomposition of hydrogen peroxide is prevented by
(a) NaOH (b) MnO_2
(c) glycerol (d) oxalic acid

A24. The oxidation number of oxygen in hydrogen peroxide is
(a) + 1 (b) – 1
(c) + 2 (d) – 2

A25. The strength of 20 volume of H_2O_2 is
(a) 13.6 g/litre (b) 60.7 g/litre
(c) 160 g/litre (d) 20.2 g/litre

A26. Hydrogen peroxide is used as an antiseptic under the name
(a) Bleaching powder (b) Perhydrol
(c) Nessler's reagent (d) Catechol

A27. 25 volumes of H_2O_2 means
(a) 25% H_2O_2
(b) 25 cm^3 of the solution contains 1g of H_2O_2
(c) 1 cm^3 of solution liberates 25 cm^3 of O_2 at N.T.P.
(d) 25 cm^3 of the solution contains 1 mole of H_2O_2.

A28. The volume strength of 1.5 N H_2O_2 solution is
(a) 4.8 (b) 8.4
(c) 3.0 (d) 8.0

Answers

A7. (d) **A8.** (d) **A9.** (d) **A10.** (d) **A11.** (b) **A12.** (d) **A13.** (b) **A14.** (b) **A15.** (c) **A16.** (b)
A17.(d) **A18.** (c) **A19.** (a) **A20.** (c) **A21.** (b) **A22.** (b) **A23.** (c) **A24.** (b) **A25.** (b) **A26.** (b)
A27.(c) **A28.** (b)

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A29. The oxide which gives H_2O_2 on treatment with dilute acid is
(a) PbO_2 (b) Na_2O_2
(c) MnO_2 (d) TiO_2

A30. The structure of H_2O_2 is
(a) Planar (b) Non-planar
(c) spherical (d) linear

A31. The O–O–H bond angle in H_2O_2 is ?
(a) 106° (b) 109°.28'
(c) 120° (d) 101.9°

A32. Which of the following equation depicts reducing nature of H_2O_2 ?
(a) $2[Fe(CN)_6]^{4-} + 2H^+ + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$
(b) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$
(c) $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$
(d) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

A33. Commercial 11.2 volume H_2O_2 solution has a molarity of
(a) 1.0 (b) 0.5
(c) 11.2 (d) 1.12

A34. H_2O_2 acts as an oxidising agent in
(a) neutral medium
(b) acidic medium
(c) alkaline and neutral medium
(d) acidic and alkaline medium

A35. What is false about H_2O_2 ?
(a) It acts as both oxidising and reducing agent
(b) Two OH bonds lie in the same plane
(c) It is pale blue liquid
(d) It can be oxidised by O_3

Answers

A29. (b) **A30.** (b) **A31.** (d) **A32.** (b) **A33.** (a) **A34.** (d) **A35.** (b)

B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT & Other State Boards' Medical Entrance

B1. The degree of hardness of water is usually expressed in terms of
(a) ppm by weight of $MgSO_4$
(b) g/L of $CaCO_3$ and $MgCO_3$ present
(c) ppm by weight of $CaCO_3$ irrespective of whether it is actually present
(d) ppm of $CaCO_3$ actually present in water
(A.M.U. Med. 2010)

B2. Permanent hardness of water is due to the presence of
(a) bicarbonates of sodium and potassium
(b) chlorides and sulphates of sodium and potassium
(c) chlorides and sulphates of calcium and magnesium
(d) bicarbonates of calcium and magnesium
(e) phosphates of sodium and potassium
(Kerala PMT 2011)

B3. Syngas is a mixture of
(a) $CO_2 + H_2$ (b) $CO + H_2$
(c) $CO + CO_2$ (d) $CO + N_2$
(e) $CO + O_2$
(Kerala P.M.T. 2012)

B4. The strength of H_2O_2 (in g/litre) in 11.2 volume solution of H_2O_2 is
(a) 17 (b) 51
(c) 34 (d) 85
(e) 68 *(Kerala P.M.T. 2012)*

B5. The inorganic compound obtained by the auto-oxidation of 2-alkylanthraquinol is
(a) H_2O (b) H_2O_2
(c) H_2 (d) O_2
(e) H_2SO_4 *(Kerala P.M.T. 2014)*

B6. (i) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
(ii) $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + 2O_2$
Role of hydrogen peroxide in the above reactions is respectively
(a) oxidising in (i) and reducing in (ii)
(b) reducing in (i) and oxidising in (ii)
(c) reducing in (i) and (ii)
(d) oxidising in (i) and (ii) *(AIPMT 2014)*

B7. Which of the following statements about hydrogen is **incorrect**?
(a) Hydrogen has three isotopes of which tritium is the most common.
(b) Hydrogen never acts as cation in ionic salts.
(c) Hydronium ion, H_3O^+ exists freely in solution.
(d) Dihydrogen does not act as reducing agent.
(NEET 2016)

Answers

B1. (c) **B2.** (c) **B3.** (b) **B4.** (c) **B5.** (b) **B6.** (c) **B7.** (a, d)

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JEE (Main) & Other State Boards' Engineering Entrance

B8. Which one of the following processes will produce hard water?
(a) Addition of Na_2SO_4 to water
(b) Saturation of water with $CaCO_3$
(c) Saturation of water with $MgCO_3$
(d) Saturation of water with $CaSO_4$ *(A.I.E.E.E. 2003)*

B9. The reagent commonly used to determine hardness of water titrimetrically is ?
(a) Oxalic acid (b) Disodium salt of EDTA
(c) Sodium citrate (d) Sodium thiosulphate *(A.I.E.E.E. 2003)*

B10. Which of the following is a true peroxide?
(a) NO_2 (b) MnO_2
(c) BaO_2 (d) SO_2 *(D.C.E. 2005)*

B11. One mole of magnesium nitride on reaction with excess of water gives
(a) one mole of ammonia
(b) one mole of nitric acid
(c) two moles of ammonia
(d) two moles of nitric acid *(A.I.E.E.E. 2004)*

B12. A commercial sample of hydrogen peroxide is labelled as 10 volume. Its percentage strength is nearly
(a) 3% (b) 1%
(c) 9% (d) 10% *(Karnataka C.E.T. 2007)*

B13. Pure water does not conduct electricity because it is
(a) basic (b) almost not ionized
(c) decomposed easily (d) acidic *(J.K. C.E.T. 2007)*

B14. Al_4C_3 on hydrolysis gives ..... gas
(a) CH_4 (b) C_2H_6
(c) C_2H_4 (d) C_2H_2 *(Orissa J.E.E. 2007)*

B15. Which of the following is formed by the action of water on Na_2O_2 ?
(a) H_2 (b) O_2
(c) N_2 (d) CO_2 *(B.H.U. 2007)*

B16. In transforming 1 mole of PbS to $PbSO_4$ the volume of '10 volume' H_2O_2 required will be
(a) 11.2 mL (b) 22.4 mL
(c) 33.6 mL (d) 44.8 mL *(WB-JEE 2008)*

B17. In context with the industrial preparation of hydrogen from water gas ($CO + H_2$), which of the following is the correct statement?
(a) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali
(b) CO and H_2 are fractionally separated using differences in their densities
(c) CO is removed by absorption in aqueous Cu_2Cl_2 solution
(d) H_2 is removed through occlusion with Pd. *(AIEEE 2008)*

B18. The strength of 10 vol. H_2O_2 solution is
(a) 10 (b) 68
(c) 60.70 (d) 30.36 *(A.M.U. Engg. 2009)*

B19. Ortho- and para-hydrogen have
(a) identical chemical properties but different physical properties
(b) identical physical and chemical properties
(c) identical physical properties but different chemical properties
(d) different physical and chemical properties *(West Bengal JEE 2010)*

B20. Why do calcium ions make water hard but sodium ions do not ?
(a) Calcium forms insoluble compounds with stearate ions present in soap
(b) Sodium forms insoluble compounds with stearate ions present in soap.
(c) Calcium forms soluble compounds with stearate ions present in soap.
(d) Both calcium and sodium form insoluble compounds with stearate ions present in soap. *(J.K. CET 2010)*

B21. Which one of the following undergoes reduction with hydrogen peroxide in an alkaline medium ?
(a) Mn^{2+} (b) HOCl
(c) PbS (d) Fe^{2+}
(e) I_2 *(Kerala PET 2010)*

B22. The normality of 30 volume H_2O_2 is
(a) 2.678 N (b) 5.336 N
(c) 8.034 N (d) 6.685 N *(WB JEE 2011)*

B23. Very pure hydrogen (99.9%) can be made by which of the following processes ?
(a) Mixing natural hydrocarbons of high molecular weight.
(b) Electrolysis of water.
(c) Reaction of salt like hydrides with water.
(d) Reaction of methane with steam. *(A.I.E.E.E. 2012)*

B24. Commercial sample of H_2O_2 is labeled as 10 V. Its % strength is nearly
(a) 3 (b) 6
(c) 9 (d) 12 *(WB. JEE 2014)*

Answers

B8. (d) **B9.** (b) **B10.** (c) **B11.** (c) **B12.** (a) **B13.** (b) **B14.** (a) **B15.** (b) **B16.** (d) **B17.** (a)
B18. (d) **B19.** (a) **B20.** (a) **B21.** (b) **B22.** (b) **B23.** (c) **B24.** (a)

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B25. In which of the following reactions, H_2O_2, acts as a reducing agent?

(1) $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

(2) $H_2O_2 - 2e^- \longrightarrow O_2 + 2H^+$

(3) $H_2O_2 + 2e^- \longrightarrow 2OH^-$

(4) $H_2O_2 + 2OH^- - 2e^- \longrightarrow O_2 + 2H_2O$

(*a*) (2), (4) (*b*) (1), (2)

(*c*) (3), (4) (*d*) (1), (3) *(JEE Main 2014)*

B26. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (Mol. wt. 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin?

(*a*) $\frac{2}{309}$ (*b*) $\frac{1}{412}$

(*c*) $\frac{1}{103}$ (*d*) $\frac{1}{206}$ *(JEE Main 2015)*

B27. From the following statements regarding H_2O_2, choose the incorrect statement.

(*a*) It has to be stored in plastic or wax lined glass bottles in dark.

(*b*) It has to be kept away from dust.

(*c*) It can act only as an oxidizing agent.

(*d*) It decomposes on exposure to light.

(JEE Main 2015)

B28. The various types of hydrides and examples of each type are given below:

Hydride type	Compound
(A) Electron deficient	(*i*) Li H
(B) Saline	(*ii*) CH_4
(C) Electron precise	(*iii*) NH_3
(D) Interstitial	(*iv*) B_2H_6
(E) Electron rich	(*v*) C_rH

Choose the correct matching from the codes given below:

(*a*) A–(*ii*), (B)–(*iv*), (C)–(*v*), (D)–(*iii*), (E)–(*i*)

(*b*) A–(*iv*), (B)–(*i*), (C)–(*ii*), (D)–(*v*), (E)–(*iii*)

(*c*) A–(*iv*), (B)–(*iii*), (C)–(*v*), (D)–(*ii*), (E)–(*i*)

(*d*) A–(*v*), (B)–(*iii*), (C)–(*iv*), (D)–(*ii*), (E)–(*i*)

(*e*) A–(*iv*), (B)–(*v*), (C)–(*i*), (D)–(*ii*), (E)–(*iii*)

(Karala PET 2016)

B29. Which one of the following statement about water is **false?**

(*a*) Water is oxidised to oxygen during photosynthesis.

(*b*) Water can act both as an acid and as a base.

(*c*) There is extensive intramolecular hydrogen bonding in the condensed phase.

(*d*) Ice formed by heavy water sinks in normal water.

(JEE Main 2015)

B30. In the manufacture of hydrogen from water gas ($CO + H_2$), which of the following is correct statement?

(*a*) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali.

(*b*) H_2 is removed by occlusion with Pd.

(*c*) Hydrogen is isolated by diffusion.

(*d*) CO and H_2 are separated based on difference in their densities.

(Karnataka CET 2017)

B31. Water gas is produced by

(*a*) passing steam over red hot coke.

(*b*) passing steam and air over red hot coke.

(*c*) burning coke in excess air.

(*d*) burning coke in limited supply of air.

(*e*) both (*a*) and (*b*).

(Kerala PET 2017)

B32. The volume of oxygen liberated at STP from 15 mL of 20 volume H_2O_2 is

(*a*) 100 mL (*b*) 150 mL

(*c*) 200 mL (*d*) 250 mL

(*e*) 300 mL *(Kerala PET 2017)*

B33. Which of the following ions will cause hardness in water?

(*a*) Ca^{2+} (*b*) Na^+

(*c*) Cl^- (*d*) K^+

(Karnataka CET 2018)

B34. H_2O_2 is

(*a*) an oxidising agent

(*b*) a reducing agent

(*c*) both oxidising and reducing agent

(*d*) neither oxdising nor reducing agent.

(Karnataka CET 2018)

B35. Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively:

(*a*) ($H_2O + O_2$) and H_2O

(*b*) ($H_2O + O_2$) and ($H_2O + OH^-$)

(*c*) H_2O and ($H_2O + O_2$)

(*d*) H_2O and ($H_2O + OH^-$) *(JEE Main 2018)*

B36. The volume strength of 1M H_2O_2 is (molar mass of H_2O_2 = 34 g mol^{-1})

(*a*) 16.8 (*b*) 11.35

(*c*) 22.4 (*d*) 5.6 *(JEE Main 2019)*

Answers

B25. (*a*) **B26.** (*b*) **B27.** (*c*) **B28.** (*b*) **B29.** (*c*) **B30.** (*a*) **B31.** (*a*) **B32.** (*e*) **B33.** (*a*) **B34.** (*c*) **B35.** (*c*) **B36.** (*b*)

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JEE (Advance) for IIT Entrance

B37. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is
(*a*) H_2O because of hydrogen bonding
(*b*) H_2Te because of higher molecular weight
(*c*) H_2S because of hydrogen bonding
(*d*) H_2Se because of lower molecular weight.
(I.I.T. 2000)

B38. Polyphosphates are used as water softening agents because they
(*a*) form soluble complexes with anionic species
(*b*) precipitate anionic species
(*c*) form soluble complexes with cationic species
(*d*) precipitate cationic species *(I.I.T. 2002)*

B39. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a
(*a*) reducing agent, oxidising agent
(*b*) reducing agent, reducing agent
(*c*) oxidising agent, oxidising agent
(*d*) oxidising agent, reducing agent *[JEE (advance) 2014]*

Answers

B37. (*a*) **B38.** (*c*) **B39.** (*a*)

C MULTIPLE CHOICE QUESTIONS *with more than one correct answer*

C1. Which of the following has larger value for D_2O than for H_2O ?
(*a*) Molecular mass (*b*) Dielectric constant
(*c*) Viscosity (*d*) Ionisation constant

C2. Molecular hydrides are
(*a*) NaH (*b*) H_2S
(*c*) LaH (*d*) HF

C3. The hydrides of which elements are non stoichiometric?
(*a*) Zirconium (*b*) Titanium
(*c*) Calcium (*d*) Sulphur

C4. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with
(*a*) H^+ ions (*b*) Ca^{2+} ions
(*c*) SO_4^{2-} ions (*d*) Mg^{2+} ions
(*e*) OH^- ions

C5. Which of the following statements are not correct ?
(*a*) Aluminium carbide reacts with heavy water to give deutero acetylene.
(*b*) In hydrated copper sulphate, four water molecules are coordinated to Cu^{2+} ion
(*c*) P_4O_{10} reacts with water to give phosphoric acid.
(*d*) H_2O_2 acts both as an oxidant as well as reductant.

C6. Which of the following statements (*s*) is/are correct in the case of heavy water ?
(*a*) Heavy water is used as a moderator in nuclear reactor.
(*b*) Heavy water is more effective as solvent than ordinary water.
(*c*) Heavy water is more associated than ordinary water.
(*d*) Heavy water has lower boiling point than orinary water.
(NCERT Exemplar Problem)

C7. Permanent hardness is due to the presence of
(*a*) Chlorides of Ca and Mg in water.
(*b*) Sulphates of Ca and Mg in water.
(*c*) Hydrogen carbonates of Ca and Mg in water
(*d*) Carbonates of alkali metals in water
(NCERT Exemplar Problem)

C8. Which of the following statements is correct ?
(*a*) Metallic hydrides are deficient of hydrogen.
(*b*) Metallic hydrides conduct heat and electricity.
(*c*) Ionic hydrides do not conduct electricity in solid state.
(*d*) Ionic hydrides are very good conductors of electricity in solid state.

C9. Which of the following statements about hydrogen are correct ?
(*a*) Hydrogen has three isotopes of which protium is the most common.
(*b*) Hydrogen never acts as cation in ionic salts.
(*c*) Hydrogen ion, H^+, exists freely in solution.
(*d*) Dihydrogen does not act as a reducing agent.

C10. Which of the following statements is correct ?
(*a*) Elements of group 15 form electron deficient hydrides.
(*b*) All elements of group 14 form electron precise hydrides.
(*c*) Electron precise hydrides have tetrahedral geometries.
(*d*) Electron rich hydrides can act as Lewis acids.

Answers

C1. (*a, c*) **C2.** (*b, d*) **C3.** (*a, b*) **C4.** (*b, d*) **C5.** (*b, c*) **C6.** (*a, c*) **C7.** (*a, d*) **C8.** (*a, b, c*) **C9.** (*a, b*) **C10.** (*b ,c*)

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NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Hydrogen resembles halogens in many respects for which several factors are responsible. Of the following factors which one is most important in this respect ?

(*a*) Its tendency to lose an electron to form a cation.
(*b*) Its tendency to gain a single electron in its valence shell to attain stable electronic configuration.
(*c*) Its low negative electron gain enthalpy value.
(*d*) Its small size.

2. Why does H^+ ion always get associated with other atoms or molecules ?

(*a*) Ionisation enthalpy of hydrogen resembles that of alkali metals.
(*b*) Its reactivity is similar to halogens.
(*c*) It resembles both alkali metals and halogens.
(*d*) Loss of an electron from hydrogen atom results in a nucleus of very small size as compared to other atoms or ions. Due to small size it cannot exist free.

3. Metal hydrides are ionic, covalent or molecular in nature. Among LiH, NaH, KH, RbH, CsH, the correct order of increasing ionic character is

(*a*) LiH > NaH > CsH > KH > RbH
(*b*) LiH < NaH < KH < RbH < CsH
(*c*) RbH > CsH > NaH > KH > LiH
(*d*) NaH > CsH > RbH > LiH > KH

4. Which of the following hydrides is electron-precise hydride ?

(*a*) B_2H_6 (*b*) NH_3
(*c*) H_2O (*d*) CH_4

5. Radioactive elements emit α, β and γ rays and are characterised by their half-lives. The radioactive isotope of hydrogen is

(*a*) Protium (*b*) Deuterium
(*c*) Tritium (*d*) Hydronium

6. Consider the reactions

(A) $H_2O_2 + 2HI \longrightarrow I_2 + 2H_2O$

(B) $HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$

Which of the following statement is correct about H_2O_2 with reference to these reactions ? Hydrogen peroxide is .....

(*a*) an oxidising agent in both (A) and (B)
(*b*) an oxidising agent in (A) and reducing agent in (B)
(*c*) a reducing agent in (A) and oxidising agent in (B)
(*d*) a reducing agent in both (A) and (B)

7. The oxide that gives H_2O_2 on treatment with dilute H_2SO_4 is

(*a*) PbO_2 (*b*) $BaO_2 \cdot 8H_2O$
(*c*) MnO_2 (*d*) TiO_2

8. Which of the following equation depicts the oxidising nature of H_2O_2 ?

(*a*) $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$
(*b*) $2Fe^{3+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{2+} + 2H_2O + O_2$
(*c*) $2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O$
(*d*) $KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$

9. Which of the following equation depicts reducing nature of H_2O_2 ?

(*a*) $2[Fe(CN)_6]^{4-} + 2H^+ + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$
(*b*) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$
(*c*) $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$
(*d*) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

10. Hydrogen peroxide is .....

(*a*) an oxidising agent
(*b*) a reducing agent
(*c*) both an oxidising and a reducing agent
(*d*) neither oxidising nor reducing agent

11. Which of the following reaction increases production of dihydrogen from synthesis gas ?

(*a*) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270K} CO(g) + 3H_2(g)$

(*b*) $C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$

(*c*) $CO(g) + H_2O(g) \xrightarrow[Catalyst]{673K} CO_2(g) + H_2(g)$

(*d*) $C_2H_6 + 2H_2O \xrightarrow[Ni]{1270K} 2CO + 5H_2$

12. When sodium peroxide is treated with dilute sulphuric acid, we get .....

(*a*) sodium sulphate and water
(*b*) sodium sulphate and oxygen
(*c*) sodium sulphate, hydrogen and oxygen
(*d*) sodium sulphate and hydrogen peroxide

Answers

1. (*b*) **2.** (*d*) **3.** (*b*) **4.** (*d*) **5.** (*c*) **6.** (*b*) **7.** (*b*) **8.** (*c*) **9.** (*b*) **10.** (*c*)
11. (*c*) **12.** (*d*)

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13. Hydrogen peroxide is obtained by the electrolysis of .....
(a) water (b) sulphuric acid
(c) hydrochloric acid (d) fused sodium peroxide

14. Which of the following reactions is an example of use of water gas in the synthesis of other compounds ?

(a) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270K} CO(g) + H_2(g)$

(b) $CO(g) + H_2O(g) \xrightarrow[Catalyst]{673K} CO(g) + H_2(g)$

(c) $C_nH_{2n+2} + nH_2O(g) \xrightarrow[Ni]{1270K} nCO + (2n+1)H_2$

(d) $CO(g) + 2H_2(g) \xrightarrow[catalyst]{Cobalt} CH_3OH(l)$

15. Which of the following ions will cause hardness in water sample ?
(a) Ca^{2+} (b) Na^+
(c) Cl^- (d) K^+

16. Which of the following compound is used for water softening ?
(a) $Ca_3(PO_4)_2$ (b) Na_3PO_4
(c) $Na_6P_6O_{18}$ (d) Na_2HPO_4

17. Elements of which of the following group (*s*) of periodic table do not form hydrides.
(a) Groups 7, 8, 9 (b) Group 13
(c) Groups 15, 16, 17 (d) Group 14

18. Only one element of ..... forms hydride.
(a) group 6 (b) group 7
(c) group 8 (d) group 9

Multiple Choice Questions (Type-II)

19. Which of the following statements are **not** true for hydrogen ?
(a) It exists as diatomic molecule.
(b) It has one electron in the outermost shell.
(c) It can lose an electron to form a cation which can freely exist.
(d) It forms a large number of ionic compounds by losing an electron.

20. Dihydrogen can be prepared on commercial scale by different methods. In its preparation by the action of steam on hydrocarbons, a mixture of CO and H_2 gas is formed it is known as
(a) water gas (b) syngas
(c) producer gas (d) industrial gas

21. Which of the following statement (*s*) is/are correct in the case of heavy water ?
(a) Heavy water is used as a moderator in nuclear reactor.
(b) Heavy water is more effective as solvent than ordinary water.
(c) Heavy water is more associated than ordinary water.
(d) Heavy water has lower boiling point than ordinary water.

22. Which of the following statements about hydrogen are correct ?
(a) Hydrogen has three isotopes of which protium is the most common.
(b) Hydrogen never acts as cation in ionic salts.
(c) Hydrogen ion, H^+, exists freely in solution.
(d) Dihydrogen does not act as a reducing agent.

23. Some of the properties of water are described below. Which of them is/are not correct ?
(a) Water is known to be a universal solvent.
(b) Hydrogen bonding is present to a large extent in liquid water.
(c) There is no hydrogen bonding in the frozen state of water.
(d) Frozen water is heavier than liquid water.

24. Hardness of water may be temporary or permanent. Permanent hardness is due to the presence of
(a) Chlorides of Ca and Mg in water
(b) Sulphates of Ca and Mg in water
(c) Hydrogen carbonates of Ca and Mg in water
(d) Carbonates of alkali metals in water

25. Which of the following statements is correct ?
(a) Elements of group 15 form electron deficient hydrides.
(b) All elements of group 14 form electron-precise hydrides.
(c) Electron-precise hydrides have tetrahedral geometries.
(d) Electron rich hydrides can act as Lewis acids.

26. Which of the following statements is correct ?
(a) Hydrides of group 13 act as Lewis acids.
(b) Hydrides of group 14 are electron deficient hydrides.
(c) Hydrides of group 14 act as Lewis acids.
(d) Hydrides of group 15 act as Lewis bases.

27. Which of the following statements is correct ?
(a) Metallic hydrides are deficient of hydrogen.
(b) Metallic hydrides conduct heat and electricity.
(c) Ionic hydrides do not conduct electricity in solid state.
(d) Ionic hydrides are very good conductors of electricity in solid state.

Answers

13. (b) **14.** (d) **15.** (a) **16.** (c) **17.** (a) **18.** (a) **19.** (a, c) **20.** (a, b) **21.** (a, c) **22.** (a, b) **23.** (c, d) **24.** (a, b) **25.** (b, c) **26.** (a, d) **27.** (a, b, c)

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Matching Type Questions

28. Correlate the items listed in Column I with those listed in Column II. Find out as many correlations as you can.

Column I	*Column II*
(*i*) Synthesis gas	(*a*) $Na_2[Na_4(PO_3)_6]$
(*ii*) Dihydrogen	(*b*) Oxidising agent
(*iii*) Heavy water	(*c*) Softening of water
(*iv*) Calgon	(*d*) Reducing agent
(*v*) Hydrogen peroxide	(*e*) Stoichiometric compounds of *s*-block elements.
(*vi*) Salt like hydrides	(*f*) Prolonged electrolysis of water
	(*g*) Zn + NaOH
	(*h*) Zn + dil. H_2SO_4
	(*i*) Synthesis of methanol
	(*j*) Mixture of CO and H_2

29. Match Column I with Column II for the given properties/applications mentioned therein.

Column I	*Column II*
(*i*) H	(*a*) Used in the name of perhydrol.
(*ii*) H_2	(*b*) Can be reduced to dihydrogen by NaH.
(*iii*) H_2O	(*c*) Can be used in hydroformylation of olefin.
(*iv*) H_2O_2	(*d*) Can be used in cutting and welding.

30. Match the terms in Column I with the relevant item in Column II.

Column I	*Column II*
(*i*) Electrolysis of water produces	(*a*) atomic reactor
(*ii*) Lithium aluminium hydride is used as	(*b*) polar molecule
(*iii*) Hydrogen chloride is a	(*c*) recombines on metal surface to generate high temperature
(*iv*) Heavy water is used in	(*d*) reducing agent
(*v*) Atomic hydrogen	(*e*) hydrogen and oxygen

31. Match the items in Column I with the relevant item in Column II.

Column I	*Column II*
(*i*) Hydrogen peroxide is used as a	(*a*) zeolite
(*ii*) Used in Calgon method	(*b*) perhydrol
(*iii*) Permanent hardness of hard water is removed by	(*c*) sodium hexametaphosphate
	(*d*) propellant

Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below :

(*a*) Statements A and R both are correct and R is the correct explanation of A.
(*b*) A is correct but R is not correct.
(*c*) A and R both are correct but R is not the correct explanation of A.
(*d*) A and R both are false.

32. Assertion (A) : Permanent hardness of water is removed by treatment with washing soda.
Reason (R) : Washing soda reacts with soluble magnesium and calcium sulphate to form insoluble carbonates.

33. Assertion (A) : Some metals like platinum and palladium can be used as storage media for hydrogen.
Reason (R) : Platinum and palladium can absorb large volumes of hydrogen.

Answers

28. (*i*) – (*i*, *j*); (*ii*) – (*b*, *d*, *e*, *g*, *h*, *i*); (*iii*) – (*f*); (*iv*) – (*a*, *c*); (*v*) – (*b*, *d*); (*vi*) – (*e*) **29.** (*i*) – (*d*); (*ii*) – (*c*); (*iii*) – (*b*); (*iv*) – (*a*)
30. (*i*) – (*e*); (*ii*) – (*d*); (*iii*) – (*b*); (*iv*) – (*a*); (*v*) – (*c*) **31.** (*i*) – (*b*, *d*); (*ii*) – (*c*); (*iii*) – (*a*, *c*) **32.** (*a*) **33.** (*a*)

Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A2. (*d*) : Cu cannot displace H_2 from dilute hydrochloric acid because it is below hydrogen in electrochemical series.

A12. (*d*) : $CO + 2H_2 \xrightarrow{\text{Catalyst}} CH_3OH$

A13. (*b*) : $Ca_3P_2 + 6H_2 \longrightarrow 3Ca(OH)_2 + 2\,PH_3$

A15. (*c*) : $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
1 mol 2 mol

A22. (*b*) : 1 L of 1 M solution of H_2O_2 contain 34 g
1 L of 3 M solution of H_2O_2 contain = 3×34 = 102g

A24. (*b*) : H_2O_2 : $1 \times 2 + 2x = 0$ $\therefore x = -1$

A25. (*b*) : $2H_2O_2 \longrightarrow 2H_2O + O_2$
$2 \times 34 = 68$ 22.4 L at N.T.P.
22.4 L of O_2 at N.T.P. is produced from 68 g H_2O_2
20 L of O_2 at N.T.P. is produced from H_2O_2

$$= \frac{68 \times 20}{22.4} = 60.7\text{g}$$

$\therefore$ Strength of H_2O_2 in 20 volume H_2O_2 = 60.7 g/L

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A28. (*b*) : Strength of $H_2O_2 = 1.5 \times 17 = 25.5g$

$2H_2O_2 \longrightarrow 2H_2O + O_2$

68 g 22.4 L

68 g of H_2O_2 give O_2 = 22.4 L

25.5 g of H_2O_2 give $O_2 = \frac{22.4}{68} \times 25.5$

= 8.4 L

Volume strength = 8.4 L **= 8.4 volumes.**

A33. (*a*): $2H_2O_2 \longrightarrow 2H_2O + O_2$

68g 22.4 L

22.4 L of O_2 at N.T.P. is produced from $H_2O_2 = 68$ g

11.2 L of O_2 at N.T.P. is produced from H_2O_2

$= \frac{68}{22.4} \times 11.2 = 34g$

Moles of $H_2O_2 = \frac{34}{34} = 1$ mol

Molarity $= \frac{1}{1} = 1M$

B. *mcq from competitive examinations*

B4. (*c*) : 11.2 volume solution means that 1L of this solution liberates 11.2 L of O_2 at N.T.P.

$2H_2O_2 \longrightarrow 2H_2O + O_2$

68g 22.4L

22.4 L of O_2 at N.T.P. is produced from H_2O_2 = 68 g

11.2 L of O_2 at N.T.P. is produced from H_2O_2

$= \frac{68}{22.4} \times 11.2 = 34$ g

Strength = 34 g/L

B6. (*c*) : H_2O_2 acts as reducing agent in all these reactions in which O_2 is evolved.

B7. (*a, d*) : Hydrogen has three isotopes of which tritium is radioactive and rare. Dihydrogen acts as reducing agent.

B11. (*c*) : $Mg_3N_2 + 3H_2O \longrightarrow 2NH_3 + 3MgO$

B12. (*a*) : $2H_2O_2 \longrightarrow 2H_2O + O_2$

$2 \times 34 = 68g$ 22.4 L at N.T.P.

22.4 L of O_2 at N.T.P. is produced from $H_2O_2 = 68$ g

10 L of O_2 is produced at N.T.P. from H_2O_2

$= \frac{68 \times 10}{22.4} = 30.35$ g

Strength of H_2O_2 in 10 volume H_2O_2 = 30.35 g/L or 3.035%

B14. (*a*) : $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

B15. (*b*) : $2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$

B18. (*d*) : 10 vol H_2O_2 means that 1 mL of H_2O_2 gives 10 mL of O_2 at N.T.P.

$2H_2O_2 \longrightarrow 2H_2O + O_2$

$2 \times 34 = 68$ g 22.4 L

22.4 L of O_2 is obtained at N.T.P. from H_2O_2

= 68 g

10 L of O_2 will be obtained at N.T.P. from H_2O_2

$= \frac{68}{22.4} \times 10$

= 30.36 g

$\therefore$ Strength of 10 volume H_2O_2 = 30.36 g

B21. (*b*) : $HOCl + H_2O_2 \longrightarrow HCl + H_2O + O_2$

B22. (*b*) : $2H_2O_2 \longrightarrow 2H_2O + O_2$

68 22.4 L at NTP

22.4 L of O_2 at N.T.P. is produced from H_2O_2

= 68 g

30 L of O_2 at N.T.P. is produced from H_2O_2

$= \frac{68}{22.4} \times 30$

= 91.07

$\therefore$ Strength of H_2O_2 in 30 volume H_2O_2 = 91.07 g/L

= 91.07 g

Gram equivalents of $H_2O_2 = \frac{91.07}{17} = 5.34$

Normality $= \frac{5.34}{1} = 5.34$ N.

B23. (*c*) : Very pure H_2 (99.9%) is prepared by the action of water on salt hydrides (*e.g.* NaH)

$NaH + H_2O \longrightarrow NaOH + H_2$.

B24. (*a*) $2H_2O_2 \longrightarrow 2H_2O + O_2$

68 g 22.4 L at N.T.P.

22.4 L O_2 at N.T.P. is obtained from $H_2O_2 = 68$ g

10 L O_2 at N.T.P. is obtained from H_2O_2

$= \frac{68}{22.4} \times 10$

= 30.357 g

10 vol. H_2O_2 means 1 L H_2O_2 gives 10 L O_2 at N.T.P.

$\therefore$ 30.35 g of H_2O_2 are present in 1 L (1000 mL) of H_2O_2

% Strength $= \frac{30.35}{1000} \times 100 = 3.035$

B25. (*a*) : The reducing agent itself gets oxidised (the O.N. increases).

(1) $H_2\overset{-1}{O}_2 + 2H^+ + 2e^- \longrightarrow 2H_2\overset{-2}{O}$

(2) $H_2\overset{-1}{O}_2 - 2e^- \longrightarrow \overset{0}{O}_2 + 2H^+$

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(3) $\overset{-1}{H_2O_2} + 2e^- \longrightarrow 2\overset{2-}{O}H^-$

(4) $\overset{-1}{H_2O_2} + 2OH^- - 2e^- \longrightarrow \overset{0}{O_2} + 2H_2O$

B26. (*b*) : $2C_8H_7SO_3Na + Ca^{2+} \longrightarrow (C_8H_7SO_3^-)_2\,Ca + 2Na^+$

2 mol 1 mol

2 mol of $C_8H_7SO_3Na$ require 1 mol of Ca^{2+}

2×206 g of $C_8H_7SO_3Na$ = 1 mol of Ca^{2+}

1 g of $C_8H_7SO_3Na = \frac{1}{412}$ mol

$\therefore$ Maximum uptake = $\frac{1}{412}$ mol per gram

B27. (*c*) : H_2O_2 can be reduced or oxidised. Hence, it can act as an oxidising agent as well as reducing agent.

B28. (*b*) : Electron deficient – B_2H_6
Saline – LiH
Electron precise – CH_4
Interstitial – CrH
Electron rich – NH_3

B29. (*c*) : There is extensive intermolecular hydrogen bonding in the condensed phase instead of intramolecular hydrogen bonding.

B31. (*a*) : $C + H_2O \longrightarrow \underbrace{H_2 + CO}$

Red hot coke — Steam — Water gas

B32. (*e*) : 1 L of 20 volume H_2O_2 liberates O_2 = 20 L
or 1000 mL of 20 volume H_2O_2 liberates O_2 = 20,000 mL

15 mL of 20 volume H_2O_2 liberates $O_2 = \frac{20{,}000 \times 15}{1000}$ = 300 mL

B33. (*a*) : The hardness of water is generally caused by the presence of carbonates, chlorides and sulphates of calcium and magnesium.

B35. (*c*) : $2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^+ \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$

$2[Fe(CN)_6]^{3-} + H_2O_2 + 2OH^- \longrightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$

B38. (*c*) : Polyphosphates such as sodium hexametaphosphate combines with cations (Ca^{2+} or Mg^{2+}) to form soluble complexes :

$2Ca^{2+} + Na_2[Na_4(PO_3)_6] \longrightarrow 4Na^+ + Na_2[Ca_2(PO_3)_6]$

Soluble complex

B39. (*a*) :

Reducing agent
Decrease in O.N.

$\overset{+7}{KIO_4} + H_2O_2 \longrightarrow \overset{+5}{KIO_3} + H_2O + O_2$

$\overset{+1}{NH_2OH} + 3H_2O_2 \longrightarrow \overset{+5}{HNO_3} + 4H_2O$

Increase in O.N.
Oxidising agent

NCERT Exemplar Problems: MCQ Type I

3. (*b*) : Ionic character increases as the size of the atom increases.
LiH < NaH < KH < RbH < CsH

4. (*d*) : Electron precise hydrides contain exact number of electrons to form normal covalent bonds *i.e.*, CH_4. Thus, option (*d*) is correct.

5. (*c*) : Nucleides with *n*/*p* (neutron-proton) ratio >1.5 are usually radioactive.
For example, tritium ($n = 2, p = 1$).

6. (*b*) : $\overset{+1\ -1}{H_2O_2} + 2\overset{-1}{H}I \longrightarrow \overset{0}{I_2} + \overset{+1\ -2}{2H_2O}$

O.N. of oxygen is decreased from $-1(H_2O_2)$ to $-2(H_2O)$, therefore, it is reduced and acts as an oxidising agent.

$HOCl + \overset{-1}{H_2O_2} \longrightarrow H_3O^+ + Cl^- + \overset{0}{O_2}$

O.N. of oxygen is increased from $-1(H_2O_2)$ to $0(O_2)$, therefore, it is oxidised and acts as a reducing agent.

7. (*b*) : The oxides such as BaO_2, NaO_2 which contain peroxide linkage ($^-O—O^-$ *i.e.* O_2^{2-}) on treatment with dil. H_2SO_4, give H_2O_2 but dioxides ($O = M = O$ where M is a metal) such as PbO_2, MnO_2, TiO_2 etc. donot give H_2O_2 on treatment with dil. H_2SO_4.

8. (*c*) : Only in reaction (*c*) O_2 is not evolved, and therefore, it represents the oxidising action of H_2O_2.

9. (*b*) : Only in reaction (*b*), O_2 is evolved, therefore, it represents reducing action of H_2O_2.

12. (*d*) : Na_2O_2 + dil. $H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$

17. (*a*) : The elements of groups 7, 8 and 9 donot form hydrides and hence, it is called hydride gap.

18. (*a*) : Only one element of group 6 *i.e.*, Cr forms hydride.

NCERT Exemplar Problems: MCQ Type II

20. (*a, b*) : Mixture of CO and H_2 is called water gas or syngas.

21. (*a, c*) : Heavy water is used as moderator in nuclear reactor and is more associated than water.

22. (*a, b*) : Hydrogen has three isotopes. H^+ being small in size, never exists as cation in ionic compounds.

23. (*c, d*) : There is hydrogen bonding even in frozen state of water and ice is lighter than liquid water.

25. (*b, c*) : Elements of group 14 form electron precise hydrides, which have tetrahedral structure.

27. (*a, b, c*) : Statement (*d*) is not correct. All other statements are correct.

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Unit Practice Test

for Board Examination

Time Allowed: 1 Hr. ***Maximum Marks: 25***

1. What is the trade name of hydrogen peroxide used as an antiseptic ? (1)

2. Concentrated sulphuric acid cannot be used for drying hydrogen. Why ? (1)

3. What happens when heavy water is added to calcium carbide? (1)

4. What is the mass ratio of different isotopes of hydrogen? (1)

5. Knowing the properties of H_2O and D_2O do you think that D_2O can be used for drinking purposes? (1)

6. Write chemical reactions to show the amphoteric nature of water. (2)

7. Compare the structure of H_2O and H_2O_2. (2)

8. Calculate the amount of hydrogen peroxide present in 10 mL of 25 volume solution of H_2O_2. (2)

9. Discuss the consequences of high enthalpy of H—H bond in terms of chemical reactivity of dihydrogen. (2)

10. What do you understand by (*i*) electron deficient, (*ii*) electron-precise, and (*iii*) electron-rich compounds of hydrogen ? Provide justification with suitable examples. (3)

12. Complete the following reactions :

(*a*) $Zn\ (s) + NaOH\ (aq) \longrightarrow$

(*b*) $LiH + AlCl_3 \xrightarrow{\text{Ether}}$

(*c*) $Ca_3N_2 + H_2O \longrightarrow$ (3)

12. (*a*) Write chemical equations to justify that hydrogen peroxide can act as an oxidizing as well as reducing agent.

(*b*) How does H_2O_2 behave as a bleaching agent ? (3)

13. (*a*) What causes the permanent hardness of water?

(*b*) Anhydrous BaO_2 cannot be used to prepare H_2O_2 by reacting with acid. Explain.

(*c*) What is meant by water – gas shift reaction? Explain. (3)

To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book.

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UNIT 10

s-BLOCK ELEMENTS (ALKALI AND ALKALINE EARTH METALS)

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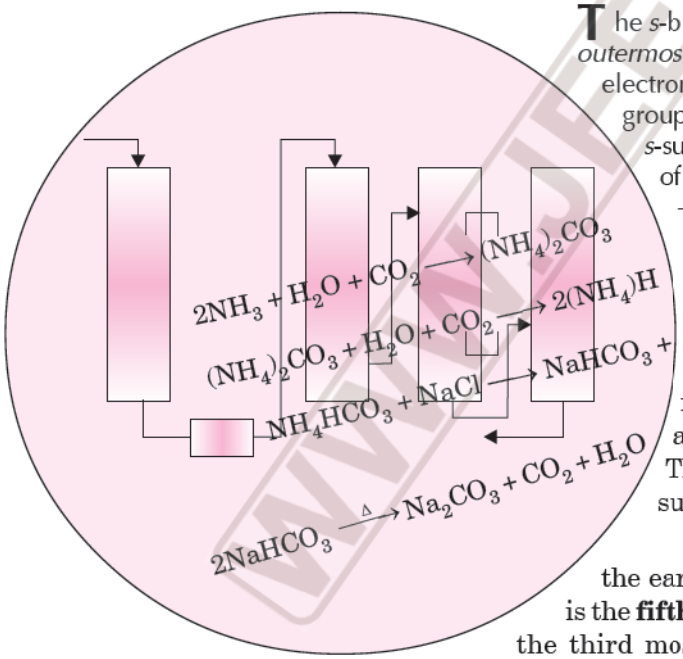
$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$
$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2(NH_4)H$
$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 +$
$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

The *s*-block elements are those *in which the last electron enters the outermost s-orbital.* As the *s*-orbital can accommodate only two electrons, this block includes only two groups; group 1 (or IA) and group 2 (or II A). They have one or two electrons in their outermost *s*-subshell respectively. These are placed on the left hand side of the Long Form of the periodic table.

The elements of group 1 are called **alkali metals** and those of group 2 are called **alkaline earth metals.** Therefore, **alkali metals and alkaline earth metals constitute *s*-block.**

ABUNDANCE AND OCCURRENCE

The alkali and alkaline earth metals are the most reactive of all the metals. These are readily oxidised and therefore, are not found in the free state in nature. These are found in the combined form with halide, oxide, sulphate, carbonate, silicate ions, etc.

The abundance of alkali and alkaline earth metals in the earth's crust shows a good range. Among these, **calcium** is the **fifth** most abundant element in the earth's crust and hence, the third most abundant metal after aluminium and iron. Vast sedimentary deposits of $CaCO_3$ occur over large parts of the earth's surface. **Magnesium** is the sixth and **sodium** is the seventh most abundant element in the crustal rocks. These are fourth and fifth most abundant metals after Al, Fe and Ca. **Potassium** (***eighth***) is the next most abundant element after sodium. Barium is fourteenth and strontium is the fifteenth most abundant element by weight in the earth's crust. Sodium and magnesium are also present in relatively large amounts in sea water, brine wells and a few salt lakes. Calcium and potassium also occur in sea water but to smaller extents. The occurrence of other metals in the earth's crust is very poor. *Francium and radium are radioactive* and have rare terrestrial abundance. Radium was

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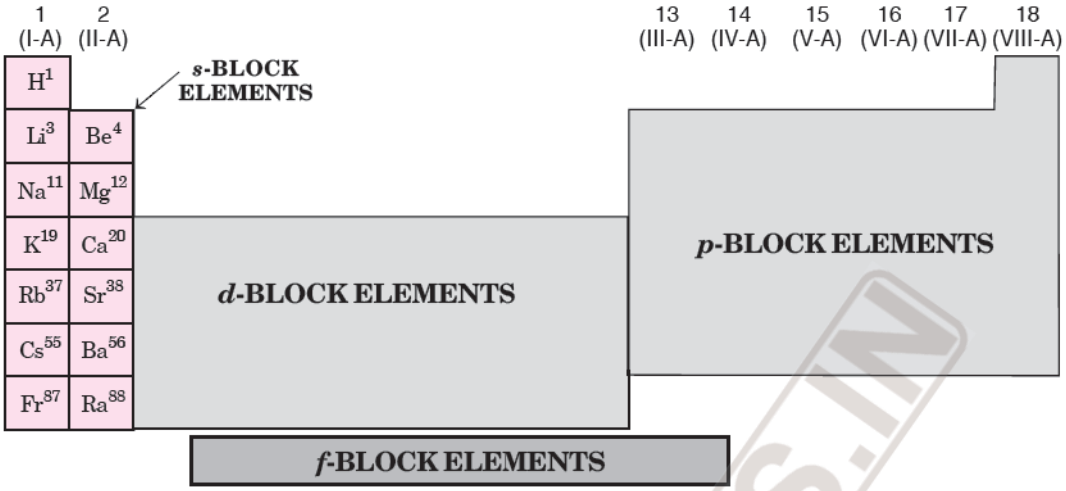

Fig. 1. *s*-block elements.

isolated by Pierre and Marie Curie by processing uranium ore pitch blende. Francium is highly radioactive and its longest lived isotope ^{223}Fr has a half-life of only 21 minutes. It is formed during radioactive decay of actinium.

$$^{227}_{89}Ac \longrightarrow {}^{223}_{87}Fr + {}^{4}_{2}He$$

Beryllium is rare and radium is the rarest of all comprising only 10^{-10} per cent of igneous rocks.

ANOMALOUS PROPERTIES OF FIRST ELEMENT IN EACH GROUP

The elements in a group show similar physical and chemical properties. However, the first member of each group differs from its succeeding members (called **congeners).** For example, lithium shows an anomalous behaviour as compared to sodium and rest of the family members of the alkali metal family. It is mainly due to the following reasons :

(*i*) Small size of the atom and its ion.
(*ii*) High ionisation enthalpy and electronegativity.
(*iii*) High polarizing power of its cation.
(*iv*) Non-availability of *d*-orbitals.

The specific characteristics differences between **lithium** and **sodium** (group 1) and **beryllium and magnesium** (group 2) are discussed later in the discussion of groups.

DIAGONAL RELATIONSHIP

It has been observed that some elements of second period show similarities with the elements of the third period present diagonally to each other, though belonging to different groups. This is called **diagonal relationship.**

Thus,
the similarity in properties of elements present diagonally is called **diagonal relationship.** This is shown in Table 1. **Three important diagonal pairs are:**
(*i*) **Lithium — magnesium**
(*ii*) **Beryllium — aluminium**
(*iii*) **Boron — silicon.**

Cause of diagonal relationship. The cause of diagonal relationship is the similarity in properties such as electronegativity, ionisation enthalpy, size or charge/radius ratio, etc. between the diagonal elements. For example, on moving from left to right across a period, the electronegativity increases and while moving down a group electronegativity decreases. Therefore, on moving diagonally, the two opposing tendencies almost cancel out and the electronegativity values remain almost same as we move diagonally. Thus, the diagonal pairs have many similar properties.

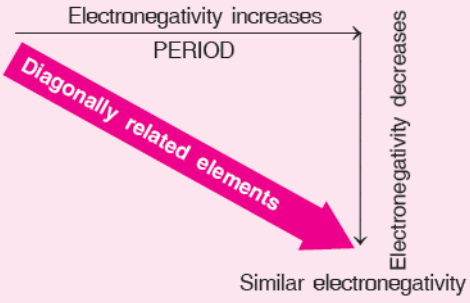

Table 1. Diagonal relationship in the periodic table.

	Group 1	Group 2	Group 13	Group 14
Second period	Li	Be	B	C
Third period	Na	Mg	Al	Si

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CHEMISTRY OF ALKALI METALS

The elements belonging to group 1 of the periodic table are called **alkali metals.** They constitute the six elements namely, *lithium* (Li), *sodium* (Na), *potassium* (K), *rubidium* (Rb), *cesium* (Cs) and *francium* (Fr). These are called **alkali metals** because they readily dissolve in water to form hydroxides which are strongly alkaline in nature. They also form alkaline oxides. The element, francium is radioactive.

OCCURRENCE

Lithium is the 35th most abundant element by weight in the earth's crust. It occurs mainly as silicate minerals such as *spodumene* [$LiAl(SiO_3)_2$], *lepidolite* [$(Li_2Al_2(SiO_3)_3(F, OH)_2$], etc.

Sodium and potassium together make up over 4% by weight of the earth's crust. Compounds of sodium and potassium have been known from ancient times. Sodium and potassium are seventh and eighth most abundant elements by weight in the earth's crust. NaCl and KCl occur in large amounts in sea water. **Rock salt** (NaCl) is the major source of sodium.

Other important minerals of sodium are: $Na_2B_4O_7.10H_2O$ (*borax*), $Na_2CO_3.NaHCO_3.2H_2O$ (*trona*), $NaNO_3$(*chile salt petre*) etc.

Potassium occurs mainly as deposits of KCl (sylvite), a mixture of KCl and NaCl (sylvinite) and double salt KCl. $MgCl_2.6H_2O$ (carnallite) and as $K_2O.Al_2O_3.6SiO_2$ (feldspar).

Rubidium and cesium are obtained as a by product of lithium processing. Francium being radioactive does not occur appreciably in nature.

GENERAL CHARACTERISTICS OF ALKALI METALS

The electronic configurations and important atomic and physical constants of alkali metals are given in Table 2 and 3 respectively. Some of these trends are discussed below.

1. Electronic Configurations

All the alkali metals have one electron in their outermost *s*-orbitals preceded by the noble gas configuration. Thus, the general configuration of alkali metals may be written as **[Noble gas]** ns^1 where n represents the valence shell. The electronic configurations of alkali metals are given in Table 2.

2. Atomic and ionic radii.

Alkali metals have the ***largest atomic*** *and* ***ionic radii*** *in their respective periods of the periodic table. On moving down the group, the atomic and ionic radii increase.*

Explanation. The alkali metals are the first elements of each period. As we move in a period, the atomic radius and ionic radius tend to decrease due to *increase in the effective nuclear charge.* Therefore, the **alkali metals have the *largest atomic and ionic* radii in their respective periods.** On moving down

Table 2. The electronic configurations of alkali metals.

Element	Symbol	Atomic No.	Electronic configuration	
Lithium	Li	3	$1s^22s^1$ or	$[He]2s^1$
Sodium	Na	11	$1s^22s^22p^63s^1$ or	$[Ne]3s^1$
Potassium	K	19	$1s^22s^22p^63s^23p^64s^1$ or	$[Ar]4s^1$
Rubidium	Rb	37	$1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1$ or	$[Kr]5s^1$
Cesium	Cs	55	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^1$ or	$[Xe]6s^1$
Francium	Fr	87	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^67s^1$ or	$[Rn]7s^1$

Table 3. Some physical properties of alkali metals.

Property	Li	Na	K	Rb	Cs	Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.94	39.10	85.47	132.91	223
Atomic radius (pm)	152	186	227	248	265	
Ionic radius (pm)	76	102	138	152	167	180
Ionization enthalpy (kJ mol^{-1})						
IE_1	520	496	419	403	376	–375
IE_2	7298	4562	3051	2633	2230	
Hydration enthalpy (kJ mol^{-1})	–506	–406	–330	–310	–276	
Electronegativity	0.98	0.93	0.82	0.82	0.79	
Density (g cm^{-3})	0.53	0.97	0.86	1.53	1.90	
Melting point (K)	454	371	336	312	302	
Boiling point (K)	1615	1156	1032	961	944.0	
E° value (V)	–3.04	–2.714	– 2.925	– 2.930	– 2.927	
$[M^+(aq) + e^- \longrightarrow M(s)]$						
Occurrence in lithosphere(ppm)	18	22700*	18400*	78	2.6	10^{-18}

*These can also be expressed as percentage by wt; Na (2.27% by wt), K (1.84% by wt), etc.

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the group, there is increase in the number of shells and, therefore, atomic and ionic radii increase.

3. Ionisation enthalpies

(*i*) *Alkali metals have the* **lowest ionisation** *enthalpy in each period. Within the group, the ionisation enthalpies of alkali metals decrease down the group.*

Explanation. The atoms of alkali metals are largest in their respective periods and therefore the valence electrons are loosely held by the nucleus. By losing the valence electron, they acquire stable noble gas configurations. Therefore, they readily lose electrons and have low ionisation enthalpies.

On moving down the group, the atomic size increases and the magnitude of screening effect (number of inner shells) also increases and consequently, the ionisation enthalpy decreases down the group.

(*ii*) *The second ionisation enthalpies of alkali metals are very high.*

Explanation. When an electron is removed from the alkali metals, they form monovalent cations which have very stable electronic configurations (same as that of noble gases). Therefore, it becomes very difficult to remove the second electron from the stable noble gas configurations and hence their second ionisation enthalpy values (IE_2) are **very high.**

Physical Properties

All the alkali metals are silver white, soft and light metals. Lithium is harder than sodium. The important characteristic physical properties (Table 3) are discussed below :

1. Melting and boiling points.

All these metals are soft and have low melting and boiling points.

Explanation. The alkali metals have only one valence electron per metal atom and therefore, the energy binding the atoms in the crystal lattice of the metal is low. Thus, the metallic bonds in these metals are not very strong and consequently, their melting and boiling points decrease on moving down from Li to Cs.

2. Density.

The densities of alkali metals are quite low as compared to other metals. Li, Na and K are even lighter than water. *The densities increase on moving down the group.* However, K is lighter than Na.

Explanation. The densities of metallic elements depend upon the type of packing of atoms in metallic state and also on their size. Because of the large size of alkali metal atoms, they have less closely packed metal atoms in their lattice. Therefore, they have low densities. As we move down the group from Li to Cs, there is increase in atomic size as well as atomic mass. But the increase in atomic mass is more than the increase in atomic size. As a result, the densities (mass/volume) of alkali metals gradually increase from Li to Cs. However, potassium is lighter than sodium probably due to abnormal increase in atomic size of potassium.

3. Electropositive or metallic character.

All the alkali metals are strongly electropositive or metallic in character.

Explanation. The electropositive character of an element is expressed in terms of the tendency of its atom to release electrons :

$$M \longrightarrow M^+ + e^-$$

As alkali metals have low ionisation enthalpies, their atoms readily lose their valence electron. These elements are, therefore, said to have strong *electropositive or metallic character.* Since the ionisation enthalpies decrease down the family, the electron releasing tendency or electropositive character is expected to increase down the family.

4. Oxidation states.

All the alkali metals exhibit an oxidation state of + 1 (unipositive ions) in their compounds.

Explanation. The alkali metals have only one electron in their valence shell and therefore they can lose the single valence electron readily to acquire the stable configuration of a noble gas. Thus, they form monovalent ions, M^+ (*e.g.*, Li^+, Na^+, K^+, Rb^+, Cs^+). Since the second ionisation enthalpies are very high, they cannot form divalent ions. Thus, alkali metals are *univalent and form ionic compounds.*

5. Characteristic flame colouration.

All the alkali metals and their salts impart characteristic flame colourations.

Explanation. The alkali metals have very low ionisation enthalpies. The energy from the flame of bunsen burner is sufficient to excite the electrons of alkali metals to higher energy levels. The excited state is quite unstable and therefore when these excited electrons come back to their original energy levels, they emit extra energy, which falls in *the visible region of the electromagnetic spectrum and thus appear coloured.*

The following colours are given by alkali metals:

	Li	Na	K	Rb	Cs
	Crimson red	Yellow	Pale violet	Violet	Bluish
λ (nm)	670.8	589.2	766.5	780.0	455.5

The different colours of the alkali metals can be explained on the basis of amount of energy absorbed for excitation of the valence electron. Therefore, the alkali metals can be detected by the respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy.

6. Photoelectric effect.

The alkali metals emit electrons when radiation strikes on their surfaces. *This phenomenon of emission of electrons when electromagnetic radiation strikes*

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against them is called **photoelectric effect** (Unit 2). Therefore, *alkali metals exhibit photoelectric effect.*

Explanation. Alkali metals have low ionisation enthalpies and therefore, the electrons are easily ejected when exposed to light. Among alkali metals, **cesium** has lowest ionisation enthalpy and hence it can show photoelectric effect to the **maximum extent.**

Because of strong photoelectric effect, cesium is frequently used in solar cells.

7. Lattice enthalpies.

The alkali metal salts consist of cations and anions which are held up by strong electrostatic forces of attraction. Therefore, *the lattice enthalpies of alkali metal salts are very high.* The lattice enthalpy is defined as the amount of energy required to break one mole of an ionic compound into its free ions.

$$MX(s) \xrightarrow{\text{Lattice enthalpy}} M^+(g) + X^-(g)$$

Therefore, lattice enthalpy gives a measure of the forces of attraction between the ions. Larger the forces of attraction, the greater will be lattice enthalpy. The lattice enthalpy also depends upon the size of the ion and its charge. *For the cation of same valency, the lattice enthalpy of ionic solids having the same anion decreases with increase in size of the cation due to decrease in forces of attraction between them.* For example,

LiCl > NaCl > KCl > RbCl > CsCl

Salt	Lattice enthalpy (kJ mol^{-1})	
LiCl	802.6	DECREASES
NaCl	758.7	
KCl	681.4	
RbCl	660.6	
CsCl	618.7	

Similarly, *the lattice enthalpy of ionic solids having the same cation decreases with increase in size of the anion as given below :*

NaF > NaCl > NaBr > NaI

Salt	Lattice enthalpy (kJ mol^{-1})	
NaF	894.5	DECREASES
NaCl	758.7	
NaBr	714.8	
NaI	668.8	

Chemical Properties

The alkali metals **exhibit high chemical reactivity.** This is due to

(i) their low ionisation enthalpies

(ii) low enthalpy of atomisation.

As the value of ionisation enthalpy decreases down the group from Li to Cs, therefore, **the reactivity of alkali metals increases from Li to Cs.**

The alkali metals are highly reactive towards the more electronegative elements such as oxygen and halogens. Some of their **characteristic chemical properties** are given below :

1. Reactivity towards air or oxygen

All alkali metals get *tarnished* in dry air due to the formation of their oxides.

When heated in excess of air or oxygen, they burn vigorously forming different types of oxides depending upon the nature of metal.

Lithium forms ***monoxide*** *(Li_2O),*
sodium forms **peroxide** *(Na_2O_2) and*
the other elements form **superoxides** *(MO_2 : M = K, Rb, Cs).*

$$4Li + O_2 \longrightarrow 2Li_2O$$
Lithium monoxide

$$2Na + O_2 \xrightarrow{575K} Na_2O_2$$
Sodium peroxide

$$M + O_2 \longrightarrow MO_2 \ (M = K, Rb, Cs)$$
Metal superoxide

Thus, **alkali metals form three types of oxides:**

(i) normal oxides containing O^{2-} ion (oxide ion)

(ii) peroxides containing O_2^{2-} ion (peroxide ion)

(iii) superoxides containing O_2^- ion (superoxide ion)

Now question arises as to why lithium forms only normal oxide, sodium forms peroxides while others form superoxides.

The formation and stability of these oxides can be explained on the basis of size of the cation (alkali metal ion) and the anion. It is known that smaller cation can stabilize smaller anion and larger cation can stabilize larger anion. This is the basis of **lattice energy effects**. The normal oxides contain O^{2-} ion, the peroxides contain O_2^{2-} [or $-O-O-]^{2-}$ ion and superoxides contain O_2^- [$:\ddot{O}\cdots\ddot{O}:]^-$ ion.

Lithium ion is very small ion and, therefore, has strong positive field around it. Therefore, it can stabilize only a small anion, O^{2-}. In other words, because of small size of lithium ion, the spreading of negative charge towards another oxygen atom is prevented and, therefore, it cannot combine with another oxygen atom to form peroxide ion, O_2^{2-}. Consequently, higher oxides are not formed. Sodium ion is large and it can stabilize large anion. The positive field around sodium ion is comparatively weaker and does not prevent the O^{2-} ion to combine with another oxygen atom to form peroxide ion, O_2^{2-}. On the other hand, because of large size of K^+, Rb^+ and Cs^+ ions, the positive field is very weak and allows even peroxide ion, O_2^{2-} to combine with another oxygen atom to form superoxide ion, O_2^-.

$$\underset{\text{Oxide}}{O^{2-}} \xrightarrow{\frac{1}{2}O_2} \underset{\text{Peroxide}}{O_2^{2-}} \xrightarrow{O_2} \underset{\text{Superoxide}}{2O_2^-}$$

2. Reactivity towards air and moisture

All alkali metals on exposure to atmosphere (air and moisture) get converted to their oxides, which react with moisture to form hydroxides and finally to

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carbonates. Therefore, alkali metals get tarnished when exposed to air and moisture.

$$4M + O_2 \longrightarrow 2M_2O$$
$$M_2O + H_2O \longrightarrow 2MOH$$
$$2MOH + CO_2 \longrightarrow M_2CO_3 + H_2O$$

Lithium shows exceptional behaviour because it reacts directly with nitrogen of air to form nitride, Li_3N.

Thus, alkali metals cannot be kept either in air or in water. **They are normally stored in inert hydrocarbon solvents like kerosene oil, petroleum ether or benzene, hexane, etc which prevent them from coming in contact with air and moisture.**

3. Reactivity towards water

Alkali metals react with water to form hydroxides, MOH and hydrogen gas is evolved.

$$2M + H_2O \longrightarrow 2M^+ + 2OH^- + H_2$$

(where M is an alkali metal)

e.g., $2Na + H_2O \longrightarrow 2Na^+ + 2OH^- + H_2$

$$2K + H_2O \longrightarrow 2K^+ + 2OH^- + H_2$$

It may be noted that although lithium has most negative E° value (Table 2), its reaction with water is less vigorous than that with sodium, which has least E° value among the alkali metals. Lithium reacts somewhat slowly. This behaviour of lithium is attributed to its small size and very high hydration energy. But sodium and the other members of the family react so explosively with water that the hydrogen gas evolved immediately catches fire.

R.U. Curious...

❑ **Sodium fire in the laboratory should not be extinguished by pouring water!**

► Sodium reacts violently with water producing H_2 gas which also catches fire. Therefore, the fire spreads instead of being extinguished. Hence, water should not be used for extinguishing sodium fire.

For extinguishing sodium fire, pyrene (CCl_4) should be used.

The hydroxides of alkali metals are strongly basic and the strength of the base increases down the group.

4. Reactivity towards hydrogen

All the alkali metals react with hydrogen at about 673 K (except Li which reacts at 1073K) to form *hydrides* which are ionic in nature (M^+H^-).

$$2M + H_2 \xrightarrow{673K} \underset{\text{Metal hydride}}{2M^+H^-} \quad (M = Na, K, Rb \text{ or } Cs)$$

$$\text{e.g., } 2Li + H_2 \xrightarrow{1073K} \underset{\text{Lithium hydride}}{2LiH}$$

$$2Na + H_2 \xrightarrow{673K} \underset{\text{Sodium hydride}}{2NaH}$$

(*i*) The **reactivity** of alkali metals with hydrogen decreases from Li to Cs as:

Li > Na > K > Rb > Cs

(*ii*) *All the alkali metal hydrides are ionic solids with high melting point. However, the ionic character of the hydrides decreases from LiH to CsH.*

(*iii*) *The stability of hydrides* **decreases** *from Li to Cs.* This is due to the fact that as the size of alkali metal increases from Li to Cs, the M—H bond becomes weak. Therefore, the stability of hydrides decreases.

(*iv*) The hydrides behave as **strong reducing agents** and their reducing nature increases down the group.

(*v*) Since these hydrides contain the hydride ion (H^-), therefore, they liberate hydrogen at the anode on electrolysis.

(*vi*) They react with proton donors such as alcohols, gaseous ammonia and alkynes liberating H_2 gas.

$$LiH(s) + H_2O(l) \longrightarrow Li(OH)(aq) + H_2(g)$$

$$\underset{\text{Alcohol}}{NaH(s) + ROH(l)} \longrightarrow \underset{\text{Sodium alkoxide}}{RONa(s)} + H_2(g)$$

$$NaH(s) + NH_3(g) \xrightarrow{\Delta} NaNH_2(s) + H_2(g)$$

$$\underset{\text{Acetyline}}{2KH(s) + HC \equiv CH(g)} \xrightarrow{\Delta} \underset{\text{Potassium acetylide}}{KC \equiv CK} + 2H_2(g)$$

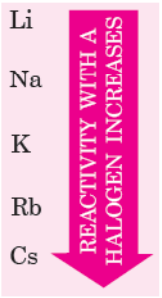
5. Reactivity towards halogens

The alkali metals readily combine with halogens to form ionic halides M^+X^- *e.g.*

$$2M + X_2 \longrightarrow 2MX \quad (X = \text{halogen})$$
$$2Na + Cl_2 \longrightarrow 2NaCl$$

The reactivity of alkali metals towards a particular halogen increases on moving down the group.

Li < Na < K < Cs



This is due to decrease in ionisation enthalpy or increase in electropositive character as we move down the group.

All the metal halides are *ionic crystals.* However, LiI is slightly covalent because of the polarization (Li^+ being the smallest cation has maximum polarizing power and iodide ion being largest anion can be polarised to the maximum extent).

6. Solutions in liquid ammonia

Alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature. As the concentration increases, the colour changes to bronze and their conductivity decreases.

Explanation. In solution, the alkali metal atom readily loses the valence electron. Both the cation and the electron combine with ammonia to form ammoniated cation and ammoniated electron.

$$M + (x + y)\,NH_3 \longrightarrow \underset{\text{Ammoniated cation}}{[M(NH_3)_x]^+} + \underset{\text{Ammoniated electron}}{[e(NH_3)_y]^-}$$

The **ammoniated electron** *is responsible for the blue colour of the solution.* When ordinary light falls on these ammoniated electrons, they get excited to higher energy levels by absorbing energy corresponding to red region of the visible light. As a result, the transmitted light is blue which imparts blue colour to the solution.

The electrical conductivity is due to the ammoniated cation as well as ammoniated electron.

The dilute solutions are paramagnetic because they contain free ammoniated electrons.

When the concentration increases, the ammoniated metal ions may get bound by free unpaired electrons.

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This is described as ***expanded metals.*** The solutions become bronze in colour and paramagnetic character decreases. The decrease in paramagnetic character suggests that in concentrated solutions the ammoniated electrons also associate to form electron pairs.

$$2e^-(NH_3)_y \longrightarrow [e^-(NH_3)_y]_2$$

Thus, blue coloured solutions (less concentrated) are *paramagnetic* while bronze coloured solutions (high concentration) are *diamagnetic.*

On standing, the solutions slowly liberate hydrogen and therefore, are unstable with respect to amide formation.

$$M^+(am) + e^-(am) + NH_3(l) \longrightarrow M\,NH_2(am) + \frac{1}{2}H_2$$

where am stands for solution in ammonia.

$$2M + 2NH_3 \longrightarrow \underset{\text{Metal amine}}{2MNH_2} + H_2O$$

However, under anhydrous conditions and in the absence of catalytic impurities (transition metals such as Fe, Pt, Zn, etc.) solutions are stable and can be stored for several days.

7. Hydration of ions

The alkali metal ions are highly hydrated. *The smaller the size of the ion, the greater is the degree of hydration.* Thus, Li^+ ion gets much more hydrated than Na^+ ion which is more hydrated than K^+ ion and so on. Therefore, the extent of hydration decreases from Li^+ to Cs^+. As a result of larger hydration of Li^+ ion than Na^+ ion, the effective size of Li^+ ion is more than that of Na^+ ion and the ionic radii in water (called hydrated ionic radii) decrease in the order :

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

Ion	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic radius (pm)	76	102	138	152	167
Hydrated radius (pm)	340	276	232	228	226
Ionic mobility ($ohm^{-1}\,cm^2\,mol^{-1}$)	33.5	43.5	64.5	67.5	68.0

As a result, **the hydrated Li^+ ion being largest in size, has the lowest mobility in water.** On the other hand, the hydrated Cs^+ ion being smallest in size has the highest mobility in water.

Li^+ has highest degree of hydration and therefore, lithium salts are mostly hydrated *e.g.*, $LiCl.\,2H_2O$.

8. Reducing nature

Alkali metals are strong reducing agents. This is due to their greater ease to lose electrons. This is also indicated by the very large negative values of their reduction potentials (Table 3). All of them are better reducing agents than hydrogen (E° = zero). Therefore, these metals react with compounds containing acidic hydrogen atoms such as alcohols and acetylene liberating hydrogen.

$$2Li + 2C_2H_5OH \longrightarrow 2C_2H_5OLi + H_2$$

$$\underset{\text{Acetylene}}{2Na + HC \equiv CH} \longrightarrow \underset{\text{Sod. acetylide}}{NaC \equiv CNa} + H_2$$

Lithium, the first element of the group is expected to be the weakest reducing agent due to its very high ionisation enthalpy. However, it is **the strongest reducing agent** *as indicated by its reduction potential value (3.04 V).* This anomaly can be explained as :

As we have learnt that ionisation is the property of isolated atoms in the gaseous state.

$$M(g) \longrightarrow M^+(g) + e^- \quad \text{Ionisation enthalpy}$$

However, oxidation potential is the property when the metal goes into the solution as $M^+(aq)$ ions :

$$M(s) \longrightarrow M^+(aq) + e^- \quad \text{Oxidation potential}$$

The process of oxidation may be thought to proceed as :

$$(i) \quad M(s) \longrightarrow M(g) \quad \Delta H \text{ sublimation}$$

$$(ii) \quad M(g) \longrightarrow M^+(g) + e^- \quad \text{Ionisation enthalpy}$$

$$(iii) \quad M^+(g) + H_2O \longrightarrow M^+(aq) \quad \text{Hydration enthalpy}$$

The overall tendency for the change depends upon the *net effect of three steps.* Now, we know that Li^+ has the smallest size and is hydrated to maximum extent. Therefore, large amount of energy (called hydration enthalpy) is released in the third step. *The amount of energy released (in third step) is so large that it compensates the higher energy needed to remove electron (in second step).* The net effect is that it has greater tendency to lose electrons in solution than other alkali metals and the reaction :

$$Li(s) \longrightarrow Li^+(aq) + e^- \text{ occurs easily}$$

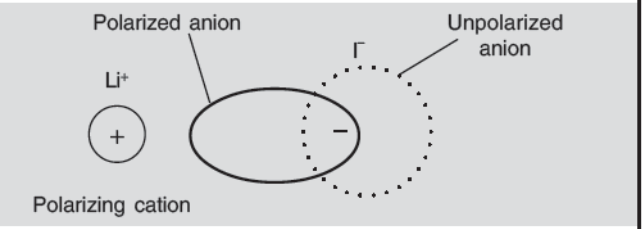
Therefore, lithium is the strongest reducing agent because of its greater hydration energy.

GENERAL CHARACTERISTICS OF THE COMPOUNDS OF ALKALI METALS

The compounds of alkali metals are mostly ionic in nature. Due to the low ionization enthalpies and large atomic sizes, the atoms of alkali metals form cations

Partial covalent character of lithium halides

The salts of alkali metals are the **most ionic salts known.** Although lithium is an alkali metal, yet its compounds, particularly halides, are slightly covalent in nature. This is because the Li^+ ion has small size and has maximum tendency to withdraw the electrons towards itself from the negative ion. In other words, it distorts the electron cloud of the anion towards itself. *This distortion of the electron cloud of the negative ion by the positive ion* is known as **polarisation.** As a result, the charges on the ions become less because some of their charges get neutralized.



This leads to covalent character. Thus, *if polarisation is more, larger will be the covalent character of the bond.* The polarisation depends upon

(*i*) *The polarisation increases with decrease in size of the cation.*

(*ii*) *The polarisation increases with increase in size of the anion* because, the anion gets polarised. If the anion is large, its electron cloud will be weakly held by the nucleus and can be easily deformed towards the cation.

(*iii*) The polarisation increases with increase in charge of the ion (cation or anion).

Thus, Li^+ being small in size, polarises the anion and results in decrease of the positive charge on Li^+ ion. Therefore, lithium halides are covalent in nature. For example, LiI is covalent.

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readily by losing the valence electrons. Consequently, they form ionic bonds with non-metals of *p*-block.

General characteristics of some of the compounds of alkali metals are discussed below.

1. Oxides and hydroxides

Alkali metals react with oxygen to form three types of oxides, namely *oxides, peroxides* and *superoxides* depending upon the metal.

Lithium forms only oxide, LiO_2 and some peroxide (Li_2O_2), sodium forms the peroxide, Na_2O_2 (plus some superoxide Na_2O) while potassium, rubidium and cesium form the superoxides (MO_2).

Under appropriate conditions, pure compounds, M_2O, M_2O_2 or MO_2 may be prepared. It may be noted that superoxide ion, $(:\ddot{O}\cdots\ddot{O}:)^-$ has three electron bond *i.e.*, it has one unpaired electron. Therefore, superoxides are coloured. For example, LiO_2 and NaO_2 are yellow, KO_2 is orange, RbO_2 is brown and CsO_2 is orange. These are also paramagnetic. Sodium peroxide is also yellow in colour probably due to the presence of some amount of superoxide in it. However, the normal oxides of alkali metals are *colourless* and *diamagnetic*.

It may be noted that the oxides of the formula M_2O_3 called **sesquoxides** have also been prepared. These are dark coloured paramagnetic powders. These are prepared by thermal decomposition of MO_2 (M = K, Rb, Cs). These can also be prepared by oxidation of liquid ammonia solutions of metals or by controlled oxidation of the peroxides. These are considered to be peroxide disuperoxides having the formula $[(M^+)_4O_2^{2-}(O_2^-)_2]$.

Alkali metals also form oxides of the formula MO_3 (called **ozonides**); M = Na, K, Rb and Cs. These ozonides on standing decompose to superoxide and oxygen.

$$2MO_3 \longrightarrow 2MO_2 + O_2$$

The normal oxides are basic because they dissolve in water to form alkali metal hydroxides. Therefore, the alkali metal oxides are **basic** in nature.

$$\underset{\text{Metal oxide}}{M_2O} + H_2O \longrightarrow 2M^+ + 2OH^-$$

e.g., $Na_2O + H_2O \longrightarrow 2NaOH\,(aq)$

Peroxides and superoxides give hydrogen peroxide also.

$$\underset{\text{Metal peroxide}}{M_2O_2} + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2O_2$$

e.g., $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

$$\underset{\text{Metal super oxide}}{2MO_2} + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

e.g., $2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

The peroxides and superoxides also act as oxidising agents because they react with water and form H_2O_2 and O_2 respectively. **Sodium peroxide is widely used as an oxidizing agent in inorganic chemistry.**

The hydroxides are obtained by the reaction of alkali metals or their oxides with water.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
$$2K + 2H_2O \longrightarrow 2KOH + H_2$$
$$Na_2O + H_2O \longrightarrow 2NaOH$$

These are white crystalline solids. *The hydroxides of alkali metals are strongly basic and their basic strength increases down the group.*

Explanation. The M—OH bond in the hydroxides of alkali metals is very weak and it can easily ionise to form M^+ and OH^- ions.

$$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq).$$

This accounts for their basic character. Since the ionisation enthalpy decreases down the group, the bond between metal and oxygen becomes weak. Therefore, the basic strength of the hydroxides increases accordingly. Thus, *NaOH is a stronger base than LiOH and so on.*

Numerous hydrates have been prepared from the aqueous solutions of the heavier alkali metal hydroxides such as $NaOH.nH_2O$ (where n = 1, 2, 3, 4, 5 and 7) but little is known about their structures.

All the hydroxides are highly soluble in water and thermally stable except lithium hydroxide which decomposes on heating to lithium oxide.

$$2LiOH \xrightarrow{\text{Heat}} Li_2O + H_2O$$

2. Halides

The alkali metal halides of the formula, MX (where M is an alkali metal and X is a halogen) are known. These are conveniently prepared by the reaction of appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). For example,

$$\underset{\text{Metal oxide}}{M_2O} + 2HX \longrightarrow 2MX + H_2O$$

$$\underset{\text{Metal hydroxide}}{MOH} + HX \longrightarrow MX + H_2O$$

$$\underset{\text{Metal carbonate}}{M_2CO_3} + 2HX \longrightarrow 2MX + CO_2 + H_2O$$

where, M = Li, Na, K, Rb or Cs and X = F, Cl, Br or I

e.g., $NaOH + HCl \longrightarrow NaCl + H_2O$

$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$

The alkali metal halides are high melting colourless crystalline solids. All these halides have high negative enthalpies of formation ($\Delta_fH°$). The enthalpies of formation for fluorides become less negative as we go down the group while the reverse is true for $\Delta_fH°$ for

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chlorides, bromides and iodides. For a given metal, the enthalpy of formation becomes less negative from the fluoride to the iodide. Thus, **fluorides of alkali metals are most stable while iodides of alkali metals are least stable**.

Table 4. Enthalpies of formation (kJ mol^{-1}) of alkali metal halides.

Element	MF	MCl	MBr	MI
Li	–612	–398	–350	–271
Na	–569	–400	–360	–288
K	–563	–428	–392	–328
Rb	–549	–423	–389	–329
Cs	–531	–424	–395	–337

The **melting and boiling points** of the alkali metal halides **decrease** with the increase in atomic mass of the halide as :

Fluoride > Chloride > Bromide > Iodide

For a given halide ion, the melting and boiling points of LiX are always less than that of NaX and their values decrease from Na to K and Rb to Cs. The values of NaX are maximum (with the exception of the m.p. of KI) for each series.

All the alkali metal halides are soluble in water with the exception of LiF. However, LiF is insoluble in water due to its high lattice energy because of small cation and small anion size. The CsI has also low solubility due to smaller hydration energy of its two ions. It may be noted that in solubilities lithium salts resemble those of Mg^{2+} salts. Other halides of lithium are soluble in ethanol, acetone, ethyl acetate etc. LiCl is soluble in pyridine.

3. Salts of oxo acids

Alkali metals are electropositive metals and therefore, they form salts with oxo acids. Oxo acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same acid. The common examples are, carbonic acid, H_2CO_3 or $OC(OH)_2$, sulphuric acid, H_2SO_4 or $O_2S(OH)_2$, phosphoric acid, H_3PO_4 or $OP(OH)_3$, etc. The alkali metals form salts with all the oxo acids. These are generally soluble in water and are thermally stable. Their carbonates (M_2CO_3) and in most cases hydrogen carbonates or bicarbonates ($MHCO_3$) are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and bicarbonates increases.

The behaviour of lithium is unusual because its carbonate is not so stable to heat and its bicarbonate does not exist as a solid. Li_2CO_3 decomposes readily because it is not very stable.

$$Li_2CO_3 \xrightarrow{\text{Heat}} Li_2O + CO_2$$

Lithium being small in size polarises a large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2.

Lithium does not form solid bicarbonate though it does exist in solution. All the other bicarbonates on gentle heating undergo decomposition to form carbonates with the evolution of carbon dioxide.

$$2MHCO_3 \xrightarrow{\text{Heat}} M_2CO_3 + CO_2 + H_2O$$

ANOMALOUS BEHAVIOUR OF LITHIUM

Though lithium belongs to the alkali metals group (Group 1) and has most of the characteristic properties of the metals of Group 1. However, it differs from the remaining members of the group in many respects. This is mainly due to the following reasons :

(i) The size of lithium atom and its ion is very small.

(ii) It has high ionisation enthalpy and least electropositive character.

(iii) The polarising power of Li^+ ion is quite high due to its small size which results in the covalent character of its compounds.

(iv) It has no vacant d-orbitals in its valence shell.

Some of the **important characteristics of distinction** between lithium and the rest of family members are given below :

(*i*) Lithium is the hardest of all the alkali metals.

(*ii*) The melting and boiling points of lithium are much higher than those of other elements of group 1.

(*iii*) Lithium is less reactive as compared to other metals and it does not get tarnished readily in air.

(*iv*) Lithium is deliquescent and crystallizes as a hydrate, $LiCl.2H_2O$ whereas, other alkali metal chlorides do not form hydrates.

(*v*) Lithium bicarbonate is not obtained in the solid form while all other elements of this group form solid bicarbonates.

(*vi*) It forms only monoxide, Li_2O with oxygen while sodium forms peroxide, Na_2O_2 and other elements form superoxide, MO_2.

(*vii*) The salts of lithium have lower ionic character than salts of other alkali metals. This is because of high polarizing power of Li^+ ion.

(*viii*) It readily reacts with nitrogen forming nitride while other metals do not react.

$$6Li + N_2 \longrightarrow 2Li_3N$$

(*ix*) Only lithium combines with carbon and silicon forming the carbide and the silicide.

(*x*) Lithium hydroxide and carbonate are unstable and decompose on heating while the corresponding compounds of the rest of the family members are stable and do not decompose :

$$2LiOH \longrightarrow Li_2O + H_2O$$

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$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

(*xi*) Upon heating, lithium nitrate gives nitrogen dioxide and oxygen.

$$4LiNO_3 \xrightarrow{Heat} \underset{\text{Nitrogen dioxide}}{2Li_2O + 4NO_2} + O_2$$

Sodium nitrate and potassium nitrate upon strong heating form corresponding nitrites and evolve oxygen.

$$2NaNO_3 \xrightarrow{Heat} 2NaNO_2 + O_2$$

(*xii*) Lithium does not react with ethyne (acetylene) to form lithium acetylide while all other alkali metals react to form corresponding acetylides. For example,

$$\underset{\text{Ethyne}}{2Na + HC{\equiv}CH} \xrightarrow[196\ K]{\text{Liq. } NH_3} \underset{\text{Disodium acetylide}}{Na^+\ {}^-C{\equiv}C^-Na^+} + H_2$$

However, when lithium is heated with carbon, it forms lithium acetylide (or lithium carbide) whereas other alkali metals do not react with carbon directly.

$$2Li + 2C \xrightarrow{Heat} \underset{\text{Dilithium acetylide}}{Li^+\ {}^-C{\equiv}C^-Li^+}$$

(*xiii*) The hydride of lithium (LiH) is more stable as compared to the hydrides of other members of the family.

(*xiv*) Lithium chloride and nitrate are soluble in alcohol, while the salts of sodium are insoluble in alcohol.

(*xv*) Lithium hydroxide is much less basic than the hydroxides of other metals.

(*xvi*) Lithium fluoride, carbonate, hydroxide, oxalate are sparingly soluble in water. The corresponding salts of sodium and potassium are readily soluble.

(*xvii*) The Li^+ ion and its compounds are more heavily hydrated than those of sodium.

DIAGONAL RELATIONSHIP OF LITHIUM WITH MAGNESIUM

As already learnt, lithium resembles with magnesium due to diagonal relationship.

Similarities of lithium and magnesium

Some **common characteristics** of lithium and magnesium are :

(*i*) The atomic radius of lithium (152 pm) is close to that of magnesium (160 pm). The ionic radii are also similar (Li^+ = 76 pm, Mg^{2+} = 72 pm).

(*ii*) Both have almost similar electronegativities (Li = 1.0, Mg = 1.2)

(*iii*) Both Li and Mg are quite hard. They are harder and lighter than other elements in the respective groups.

(*iv*) Both LiOH and $Mg(OH)_2$ are weak bases.

(*v*) Unlike the other members of the group, lithium reacts with N_2 to form lithium nitride. Magnesium also reacts in a similar way.

$$6Li + N_2 \xrightarrow{Heat} \underset{\text{Lithium nitride}}{2Li_3N}$$

$$3Mg + N_2 \xrightarrow{Heat} \underset{\text{Magnesium nitride}}{Mg_3N_2}$$

(*vi*) Both lithium and magnesium combine with oxygen to form monoxides. Other members form peroxides and superoxides.

$$4Li + O_2 \xrightarrow{Heat} 2Li_2O$$

$$2Mg + O_2 \xrightarrow{Heat} 2MgO$$

The oxides Li_2O and MgO do not combine with excess O_2 to form peroxides or superoxides.

(*vii*) Both react slowly with cold water. Their oxides and hydroxides are much less soluble. The hydroxides of both these metals decompose on strong heating to form respective oxides.

$$2LiOH \xrightarrow{Heat} Li_2O + H_2O$$

$$Mg(OH)_2 \xrightarrow{Heat} MgO + H_2O$$

(*viii*) The carbonates of both these metals decompose on heating to form oxide and evolve CO_2.

$$Li_2CO_3 \xrightarrow{Heat} Li_2O + CO_2$$

$$MgCO_3 \xrightarrow{Heat} MgO + CO_2$$

(*ix*) Solid bicarbonates of both lithium and magnesium are not formed.

(*x*) Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl.2H_2O$ and $MgCl_2.8H_2O$.

(*xi*) Both LiCl and $MgCl_2$ are soluble in ethanol.

(*xii*) The nitrates of both lithium and magnesium evolve nitrogen dioxide and oxygen on heating.

$$4LiNO_3 \xrightarrow{Heat} 2Li_2O + 4NO_2 + O_2$$

$$2Mg(NO_3)_2 \xrightarrow{Heat} 2MgO + 4NO_2 + O_2$$

(*xiii*) Lithium hydroxide, fluoride, phosphate, oxalate and carbonate are much less soluble than the corresponding sodium and potassium salts. However, the solubilities are comparable to those of the corresponding magnesium compounds.

SOLVED EXAMPLES

Example 1.

What makes lithium to show properties uncommon to rest of the alkali metals ?

Solution: The uncommon properties of lithium as compared to other alkali metals is due to

(*i*) The exceptionally small size of its atom and ion.

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(*ii*) High polarising power because of high charge/ radius of its ion.

❑ **Example 2.**

When a cation is highly polarising ? Which alkali metal ion has the highest polarising power ?

Solution: A cation is highly polarising if its charge / radius ratio is very high. Li^+ ion has the highest polarising power among the alkali metal ions because it has highest charge/ radius ratio.

❑ **Example 3.**

Arrange the following alkali metal ions in decreasing order of their mobility : Li^+, Na^+, K^+, Rb^+, Cs^+

Solution: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

❑ **Example 4.**

Arrange the following in order of increasing covalent character :

MCl, MBr, MF and MI (where M = alkali metal)

Solution: With increasing size of the anion, covalent character increases and, hence, the order is :

MF < MCl < MBr < MI.

❑ **Example 5.**

What is the oxidation state of

(i) lithium in Li_2O.

(ii) sodium in Na_2O_2.

(iii) potassium in KO_2.

Solution: (*i*) Lithium in Li_2O.

$2x + (-2) = 0 \qquad \therefore x = +1$

Oxidation state of Li in Li_2O is +1.

(*ii*) Sodium in Na_2O_2. The oxidation state of peroxide ion, O_2^{2-} is –2.

$\therefore 2x + (-2) = 0 \qquad \therefore x = +1$

Oxidation state of Na in Na_2O_2 is +1.

(*iii*) Potassium in KO_2

The oxidation state of superoxide ion, O_2^- is –1

$\therefore x + (-1) = 0$ or $x = +1$

Oxidation state of K in KO_2 is +1

❑ **Example 6.**

The E° values are :

$Cl^-/Cl_2 = +1.36V, \qquad I^-/I_2 = +0.53V$

$Ag^+/Ag = +0.79V, \quad Na^+/Na = -2.71V$

$Li^+/Li = -3.04V$

Arrange the following ionic species in decreasing order of reducing strength:

$I^-, Ag^+, Cl^-, Li^+, Na^+$ **N.C.E.R.T.**

Solution: The lesser the E° value, the stronger is the reducing agent. Therefore, the decreasing order of reducing strength is:

$Li^+ > Na^+ > I^- > Ag^+ > Cl^-$.

❑ **Example 7.**

Why is KO_2 paramagnetic? **N.C.E.R.T.**

Solution: The superoxide ion, O_2^- may be represented as:

$$[:\ddot{O}\text{-}\ddot{O}:]^-.$$

It contains one unpaired electron and therefore, it is paramagnetic. The M.O. electronic configuration of O_2^- is:

$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2\pi_y)^1$

This also shows that it has one unpaired electron and hence is paramagnetic.

USES OF ALKALI METALS

Some of the important uses of alkali metals are listed below :

Uses of lithium

The important uses of lithium are :

(*i*) It is used in the manufacture of various alloys such as lithium-lead alloy, lithium- aluminium alloy, lithium–magnesium alloy etc.

- Its alloy with magnesium (14% Li) lithium-magnesium is extremely tough and corrosion resistant. It is used for armour plate and aerospace components.
- The lithium-lead alloy (0.05% Li) (called white metal) is used for making toughened bearings for motor engines and sheets for cables.
- Lithium-aluminium alloy has high tensile strength and elasticity like that of mild steel. It is used for aircraft construction.

(*ii*) Lithium is used for refining copper and nickel.

(*iii*) Lithium is used for producing **thermo-nuclear energy** required for propelling rockets and guided missiles.

(*iv*) Lithium is used to make both primary and secondary batteries. There is great interest in Li/S batteries which could power battery cars in the future.

(*v*) Lithium compounds also find extensive uses such as :

(*a*) Lithium carbonate is used for making special variety of tough glass which is weather proof and is very strong.

(*b*) Lithium chloride is used in air-conditioning plants to regulate the humidity.

(*c*) Lithium hydride is used to generate hydrogen for meteorological purposes.

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(*d*) Lithium hydroxide is used to absorb CO_2 from exhaled air in closed quarters like submarines and space vehicles.

(*e*) Lithium bromide is used in medicines as sedative.

(*f*) Lithium stearate is used in making automobile grease.

(*g*) Lithium bicarbonate and lithium salicylate have been used for treatment of **rheumatism** because the lithium urate formed is soluble in water.

(*h*) Lithium aluminium hydride ($LiAlH_4$) is used as a reducing agent in synthetic organic chemistry.

Uses of sodium

The important uses of sodium are:

(*i*) An alloy of sodium with mercury (sodium amalgam) is used for the preparation of many organic compounds.

(*ii*) Liquid sodium or its alloy with potassium is used as a coolant in fast breeder nuclear reactors. It transfers heat from the reactor to turbines, where the heat produces steam which is used to generate electricity.

(*iii*) Sodium with lead alloy is used to prepare tetraethyl lead $(C_2H_5)_4$ Pb, which acts as an antiknock compound for petrol. About 60% of the world production of sodium is used to make $(C_2H_5)_4Pb$.

(*iv*) It is used in sodium vapour lamp.

(*v*) Sodium is used as reagent to detect the presence of nitrogen, sulphur and halogens in organic compounds (Lassaigne extract).

(*vi*) Sodium is used for the preparation of useful reagents such as $NaNH_2$ (sodamide), Na_2O_2 (sodium peroxide) and NaCN (sodium cyanide).

(*vii*) Sodium is used as a reducing agent in the extraction of boron and silicon.

(*viii*) It is used as a reagent in Wurtz reaction for the synthesis of many organic compounds. It is also used in drying organic solvents.

(*ix*) Sodium is largely used in industry for the production of artificial rubber, dyes, drugs, etc.

(*x*) Because of its lightness and high thermal conductivity, it is used for filling exhaust valves of aeroplane engines.

Uses of potassium

The important uses of potassium are :

(*i*) It is used as a fertilizer in agriculture.

(*ii*) It has vital role in biological systems.

(*iii*) It is used in the preparation of many useful potassium compounds such as

- Potassium chloride is used as a fertilizer.
- Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide.
- Potassium nitrate is used in ceramics, colour TV tubes and fluorescent light tubes.

Cesium is used in devicing photoelectric cells.

SOME IMPORTANT COMPOUNDS OF SODIUM

Sodium forms many industrially important compounds. Among these sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate are very important and are discussed below :

1. Sodium carbonate (washing soda), $Na_2CO_3.10H_2O$.

Sodium carbonate is generally prepared commercially by *Solvay process or ammonia-soda process.*

In principle, sodium carbonate may be simply prepared as :

$$2NaCl + CaCO_3 \longrightarrow Na_2CO_3 + CaCl_2$$

However, this reaction is reversible and creates other problems in the system. Therefore, other chemicals are required to get the desired product. It can be prepared on the basis of the following principle.

Principle of the process. When carbon dioxide gas is passed through a brine solution (about 28% NaCl), saturated with ammonia, it gives sodium bicarbonate.

$$2NH_3 + H_2O + CO_2 \longrightarrow \underset{\text{Ammonium carbonate}}{(NH_4)_2CO_3}$$

$$(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Ammonium bicarbonate}}{2NH_4HCO_3}$$

$$\underset{\text{Brine}}{NH_4HCO_3 + NaCl} \longrightarrow \underset{\text{Sodium bicarbonate (ppt.)}}{NaHCO_3} + NH_4Cl$$

The precipitated sodium bicarbonate is filtered and dried. It is ignited to give sodium carbonate.

$$2NaHCO_3 \xrightarrow{\text{Heat}} \underset{\text{Sodium carbonate}}{Na_2CO_3} + CO_2 + H_2O$$

Raw materials. The raw materials for the process are :

(*i*) Sodium chloride (NaCl).

(*ii*) Limestone ($CaCO_3$) for carbon dioxide.

(*iii*) Ammonia gas (NH_3).

Details of the process. The plant used for the manufacture of Na_2CO_3 is shown in Fig. 2. It involves the following steps :

1. Ammonia absorber–saturation of brine with ammonia. About 30% brine solution is pumped

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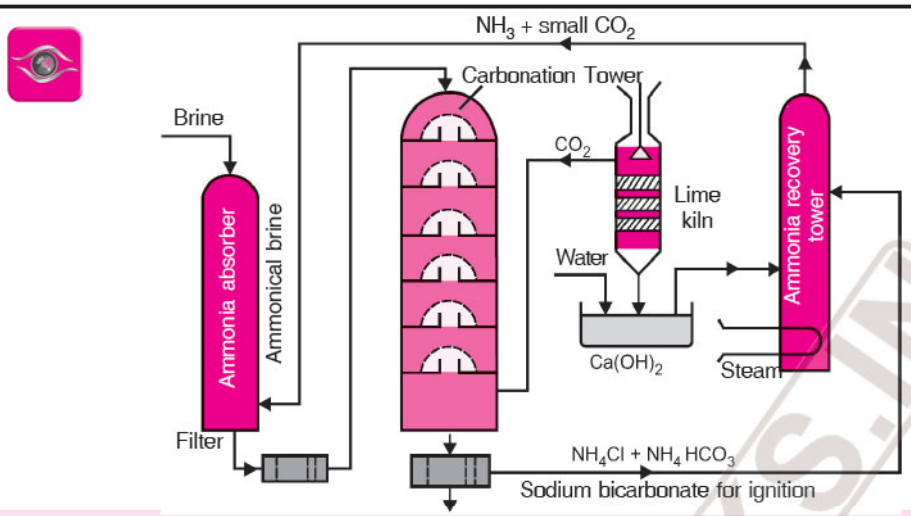

Fig. 2. Solvay process for the manufacture of Na_2CO_3.

into ammonia absorber. A mixture of ammonia and a small amount of carbon dioxide is bubbled through the brine solution so that it gets saturated with ammonia. The impurities of magnesium or calcium salts (if present in brine) are precipitated as their carbonates.

$$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$
$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 + 2NH_4Cl$$
(ppt.)
$$MgCl_2 + (NH_4)_2CO_3 \longrightarrow MgCO_3 + 2NH_4Cl$$
(ppt.)

The ammoniated brine is filtered to remove the precipitates of calcium and magnesium carbonate.

2. Carbonation tower. The ammoniated brine is introduced from the top of a tower known as **carbonation tower**. It is packed with a number of horizontal perforated plates each having a hole covered by a perforated plate. In this tower, carbon dioxide is admitted from the base of the tower, which rises through the small perforations. The brine solution slowly trickles down and meets the upgoing vapours of carbon dioxide to form insoluble sodium bicarbonate.

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$
$$Na^+ + Cl^- + NH_4^+ + OH^- + CO_2 \longrightarrow Na^+ + HCO_3^- + NH_4^+ + Cl^-$$
$$Na^+ + HCO_3^- \longrightarrow NaHCO_3$$
(as precipitate)
$$NH_4^+ + Cl^- \longrightarrow NH_4Cl$$
(in solution)

or $NaCl + NH_3 + H_2O + CO_2 \longrightarrow NaHCO_3 + NH_4Cl$
ppt. in solution

3. Filtration. The milky solution from the carbonation tower is filtered with the help of rotary vacuum pump to separate sodium bicarbonate.

The filtrate containing ammonium chloride and small amount of ammonium bicarbonate is pumped to the top of the ammonia recovery tower.

4. Calcination of sodium bicarbonate. Sodium bicarbonate recovered from the carbonation tower is heated strongly (calcined) in a kiln to form sodium carbonate.

$$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3 + H_2O + CO_2$$

5. Ammonia recovery tower. The filtrate in step-3 (containing ammonium chloride and ammonium bicarbonate) is mixed with calcium hydroxide and heated with steam in ammonia recovery tower with calcium hydroxide.

$$NH_4HCO_3 \xrightarrow{\text{Heat}} NH_3 + CO_2 + H_2O$$
$$\underset{\text{Ammonium chloride}}{2NH_4Cl} + Ca(OH)_2 \xrightarrow{\text{Heat}} CaCl_2 + 2NH_3 + 2H_2O$$

The ammonia along with a small amount of carbon dioxide is pumped to the top of the brine saturation tower as shown in the figure.

6. Lime kiln. The carbon dioxide required in carbonation tower is prepared by heating limestone ($CaCO_3$) to about 1300 K in a **lime kiln**. Lime formed is dissolved in water to get calcium hydroxide which is transferred to the ammonia recovery tower.

$$CaCO_3 \xrightarrow{\text{Heat}} \underset{\text{Calcium oxide (lime)}}{CaO} + CO_2$$
$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Properties

(*i*) Sodium carbonate is a white crystalline solid which exists as a decahydrate ($Na_2CO_3 . 10H_2O$). This is also called **washing soda.**

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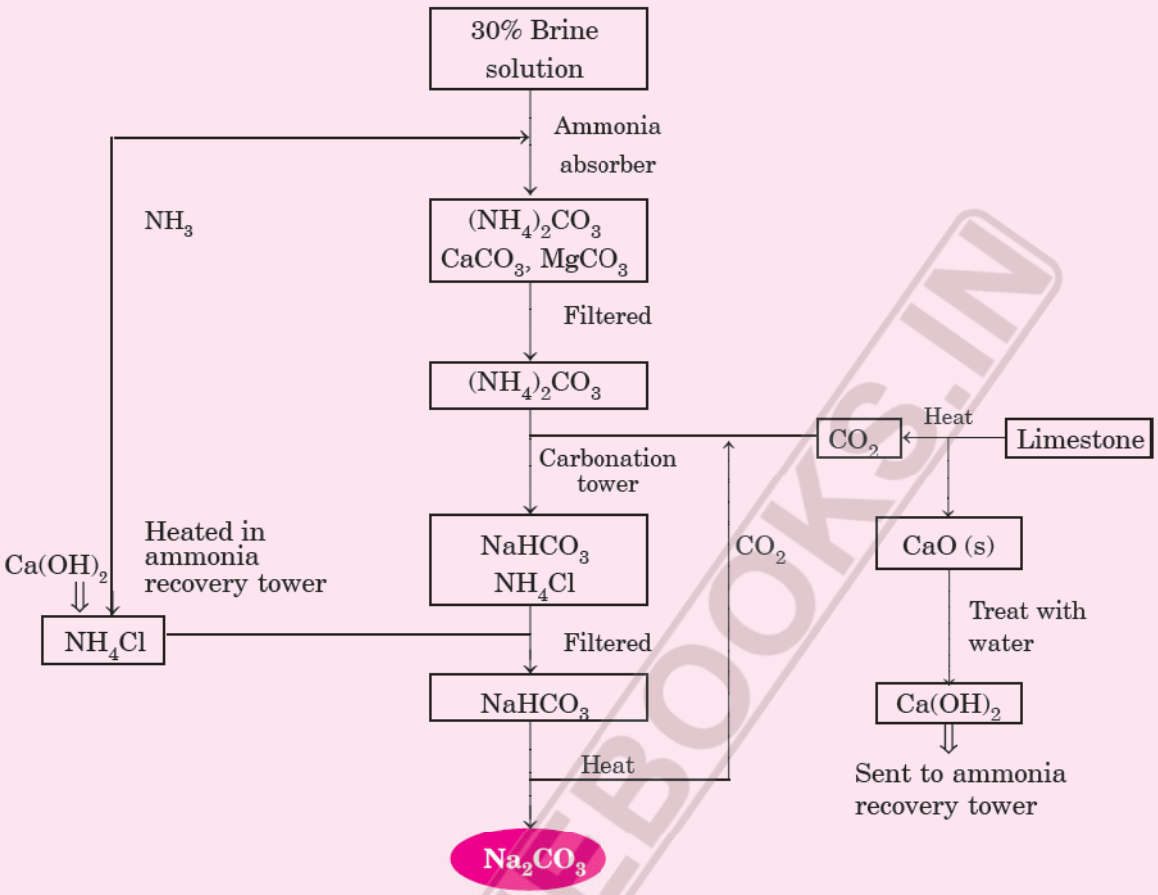
Flow sheet diagram for Solvay process :



(*ii*) It is readily soluble in water.

(*iii*) **Action of heat.** On heating, the decahydrate loses the water of crystallisation to form monohydrate ($Na_2CO_3 . H_2O$). Above 373 K, the monohydrate becomes completely anhydrous and changes to a white powder called **soda ash.**

$$Na_2CO_3 . 10H_2O \xrightarrow{373\ K} Na_2CO_3.H_2O + 9H_2O$$

$$Na_2CO_3.H_2O \xrightarrow{\text{above } 373\ K} \underset{\text{Soda ash}}{Na_2CO_3} + H_2O$$

(*iv*) **Hydrolysis.** It gets hydrolysed by water to form an alkaline solution.

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$$

(*v*) **Action of acids.** It reacts with dilute mineral acids evolving carbon dioxide gas.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

(*vi*) **Reaction with milk of lime.** With hot milk of lime, $Ca(OH)_2$, sodium carbonate reacts to form sodium hydroxide.

$$Ca(OH)_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaOH$$

(*vii*) **Reaction with carbon dioxide.** On passing CO_2 through aqueous solution of sodium carbonate, sodium hydrogen carbonate is formed.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

Uses of sodium carbonate

The important uses of sodium carbonate are :

(*i*) It is used for softening of hard water.

(*ii*) It is used for washing purposes in laundary.

(*iii*) A mixture of Na_2CO_3 and K_2CO_3 is used as a fusion mixture.

(*iv*) It is used in textile industry and also in petroleum refining.

(*v*) It is used for the manufacture of soap, glass, paper, borax, caustic soda, etc.

(*vi*) It is used as a reagent in the laboratory.

(*vii*) It is used for paint and dye stuffs.

(*viii*) It is used for metal refining.

(*ix*) It is used for the manufacture of sodium compounds such as borax, caustic soda, sodium phosphate, etc.

2. Sodium chloride, NaCl

Preparation. Sea water is the major source of sodium chloride. The sea water contains about 2.7—2.9% of NaCl. In tropical countries like India, common salt is generally obtained by evaporation of sea water. In India, about 50 lakh tons of salt are produced annually by solar evaporation. The evaporation of sea water gives crude sodium chloride which contains impurities of calcium sulphate, sodium sulphate, calcium chloride and magnesium chloride. Calcium chloride, $CaCl_2$ and magnesium chloride, $MgCl_2$ are impurities because they are deliquescent and absorb moisture easily from the atmosphere. For purification, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble

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impurities. Then HCl gas is passed through the solution to get saturated solution. Due to common ion effect, the crystals of pure sodium chloride separate out. The salts of chlorides of calcium and magnesium being more soluble in water remain in the solution.

Properties.

(*i*) It is white crystalline solid.

(*ii*) It has m.p. 1081K and b.p. 1713K.

(*iii*) It is soluble in water and its solubility is 36 g per 100 g of water at 273K.

(*iv*) Pure sodium chloride is non-hygroscopic but due to the impurities of $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 2H_2O$, it behaves as hygroscopic.

Uses of sodium chloride

(*i*) It is used as a table salt or common salt for domestic purposes, an essential constituent of our food.

(*ii*) It is used in the manufacture of Na_2O_2, Na_2CO_3, NaOH, Cl_2, etc.

(*iii*) It is used for salting out soap.

(*iv*) It is used in freezing mixture.

(*v*) It is used in tanning and textile industries.

3. Sodium hydroxide or caustic soda, NaOH

Sodium hydroxide is manufactured by the electrolysis of a saturated solution of sodium chloride (brine) in the following types of cells.

(*a*) Mercury cathode cell or Castner Kellner Cell. The cell consists of a rectangular iron tank in which mercury flows along the bottom of the cell and is made cathode. The brine solution flows in the same direction and the anode consists of a number of graphite blocks. When electric current is passed through the cell, the following reactions take place at different electrodes.

$$NaCl \longrightarrow Na^+ + Cl^-$$

At anode

$$Cl^- - e^- \longrightarrow Cl$$

$$Cl + Cl \longrightarrow Cl_2$$

or

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

At cathode

$$Na^+ + e^- \longrightarrow Na$$

$$Na + Hg \longrightarrow NaHg$$

Sodium amalgam

Since the cathode is mercury, the sodium atoms produced dissolve in mercury and form an amalgam. The sodium amalgam flows out and is reacted with water to give NaOH and H_2 gas is evolved.

$$2NaHg + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$$

The clean mercury is recycled back to the electrolysis tank. Thus during electrolysis, hydrogen is evolved at cathode and chlorine is evolved at anode. Hydrogen and chlorine are two important by products.

It may be noted that originally the anodes were made of graphite. But because of traces of oxygen produced in a side reaction, they may become pitted due to the formation of CO_2. Therefore, these days anodes are made of steel coated with titanium because, titanium is very resistant to corrosion and it prevents the problem of pitting and forming CO_2.

It also lowers the electrical resistance.

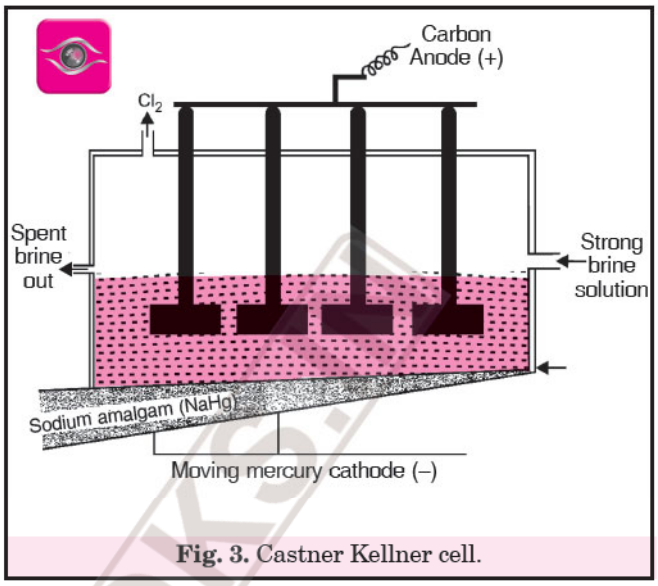

Fig. 3. Castner Kellner cell.

(*b*) Diaphragm cell. In Castner Kellner cell, there is one problem. The chlorine gas evolved at the anode tends to dissolve and react with sodium hydroxide forming sodium hypochlorite as :

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

or

$$Cl_2 + 2OH^- \longrightarrow OCl^- + H_2$$

Hypochlorite

If H_2 and Cl_2 gases mix and react, the reaction may be explosive. In the presence of sunlight, a photolytic reaction may take place which produces chlorine atoms leading to an explosive chain reaction with hydrogen. Therefore, it is essential to prevent the contact of chlorine with the solution. For this, an asbestos diaphragm is used which separates the anode and cathode compartments. This reduces the chances that NaOH produced in the cathode compartment can mix and react with Cl_2 produced in the anode compartment. Thus, it reduces the chances of the side reaction producing hypochlorite.

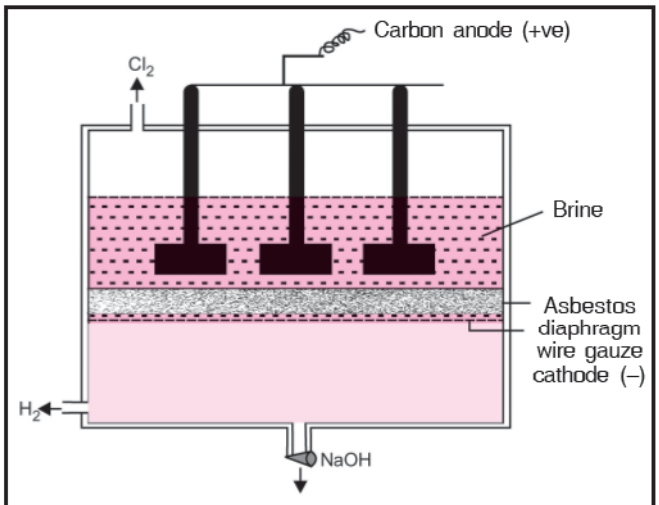

Fig. 4. Diaphragm method for manufacture of NaOH.

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When the current is passed through carbon (+ve) anode and wire gauze (–ve) cathode, electrolysis begins.

$$2NaCl\,(aq) + 2H_2O\,(l) \xrightarrow{\text{Electrolysis}} 2NaOH\,(aq) + H_2(g) + Cl_2(g)$$

Chlorine gas is produced at the carbon anode and sodium hydroxide is formed at the outside edge of the cathode.

Nafion Membrane Cell

There has been considerable interest in using thin synthetic plastic membranes as diaphragm in place of asbestos. These membranes are made of a polymer called nafion supported on a teflon mesh. Nafion is a copolymer of tetrafluoroethylene and a pentafluoro sulphonyl ethoxy ether. These plastic membranes have lower resistance than asbestos. In this cell, the natural brine is electrolysed in a membrane cell in which the anolyte and the catholyte are separated by a nafion membrane. The electrolysis occurs as :

$$2NaCl\,(aq) + 2H_2O\,(l) \xrightarrow{\text{Electrolysis}} 2NaOH\,(aq) + H_2(g) + Cl_2(g)$$

In India, about 1.35 million tonnes of caustic soda is produced annually. Presently, nafion membrane method is used in place of diaphragm.

Properties

(*i*) Sodium hydroxide is a white crystalline, deliquescent solid. It melts at 591 K.

(*ii*) It is readily soluble in water to give alkaline solution. It also neutralises acids forming salt and water.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

(*iii*) The crystals of sodium hydroxide are *deliquescent i.e.*, they absorb moisture from air. On prolong exposure, sodium hydroxide absorbs CO_2 resulting in the formation of white crust of solid hydrated Na_2CO_3 at the surface.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

(*iv*) Its aqueous solution is soapy to touch and has a strong corrosive action on the skin.

(*v*) An aqueous solution of sodium hydroxide contains large concentration of hydroxyl ions (OH^-) and precipitates insoluble metal hydroxides from solutions containing metallic ions. The hydroxides of aluminium, zinc, lead and tin dissolve in excess of sodium hydroxide giving clear solutions due to the formation of soluble complexes. These soluble complexes can also be obtained when these metals react with concentrated solution of NaOH. For example,

$$AlCl_3 + 3NaOH \longrightarrow \underset{\text{White ppt}}{Al(OH)_3} + 3\,NaCl$$

$$Al(OH)_3 + 3OH^- \longrightarrow \underset{\text{Soluble complex}}{[Al(OH)_6]^{3-}}$$

$$\text{or } 2Al + 6OH^- + 6H_2O \longrightarrow 2[Al(OH)_6]^{3-} + 3H_2$$

Similarly,

$$Zn(NO_2)_2 + 2NaOH \longrightarrow \underset{\text{ppt}}{Zn(OH)_2} + 2NaNO_3$$

$$Zn(OH)_2 + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$$

$$\text{or } Zn + 2OH^- + 2H_2O \longrightarrow [Zn(OH)_4]^{2-} + H_2$$

Uses of sodium hydroxide

(*i*) Sodium hydroxide is used in the manufacture of soap, paper, artificial silk and a number of chemicals.

(*ii*) It is used in the petroleum refining.

(*iii*) It is used in the purification of bauxite (ore of aluminium).

(*iv*) It is used in the textile industry for mercerising cotton fabrics.

(*v*) It is used as cleansing agent for machines and metal sheets.

(*vi*) It is used for the preparation of pure fats and oils.

(*vii*) It is used for the preparation of artificial silk.

4. Sodium hydrogen carbonate or Baking soda, $NaHCO_3$

Preparation.

Sodium bicarbonate is obtained as an intermediate product in Solvay's process for the manufacture of sodium carbonate.

It can also be prepared by saturating a solution of sodium carbonate with carbon dioxide. Sodium bicarbonate being less soluble separates out as white crystals.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

Properties.

(*i*) It is a white crystalline solid.

(*ii*) It is only sparingly soluble in water.

(*iii*) Upon heating to 373 K, it decomposes to form sodium carbonate.

$$2NaHCO_3 \xrightarrow{373K} Na_2CO_3 + H_2O + CO_2$$

(*iv*) Its aqueous solution is alkaline in nature.

$$NaHCO_3 + H_2O \longrightarrow NaOH + H_2O + CO_2$$

Uses of sodium hydrogen carbonate

(*i*) Sodium hydrogen carbonate (or baking soda) is mainly used in making baking powder. Baking powder contains sodium hydrogen carbonate and an acid like tartaric acid or citric acid. When baking powder (mixed in the dough for preparing cakes or bread) is heated, sodium hydrogen carbonate decomposes to give carbon dioxide and sodium carbonate. Carbon dioxide bubbles out causing the bread

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and cakes to rise leaving holes in cakes or pastries. This makes them light and fluffy. Tartaric acid or citric acid present in the baking powder reacts with sodium carbonate and neutralises it. It may be noted that *if tartaric acid or citric acid is not present in baking powder, it will taste bitter due to the presence of sodium carbonate*.

It may be noted that baking powder must be added during the preparation of cakes, pastries, etc. If, however, baking powder is not added, the cake obtained will be comparatively hard and small in size.

(*ii*) Baking soda is used in medicines as an antacid to remove acidity of the stomach. Sodium hydrogen carbonate is a mild antiseptic for skin infections.

(*iii*) It is used in the manufacture of aerated water (soda water).

(*iv*) Sodium bicarbonate is used in fire extinguishers. Soda acid fire extinguisher contains a solution of sodium hydrogen carbonate and sulphuric acid. These can be brought in contact with each other either by pressing a knob or by inverting the extinguisher. Carbon dioxide is liberated and it forces a steam of effervescing liquid on to the fire. As a result, carbon dioxide surrounds the combustible substances and cuts off the supply of air. Thus, it helps to put out the fire.

BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

Sodium and potassium are most common cations in biological systems. Though Na^+ and K^+ ions are chemically quite similar but surprisingly they differ greatly in their biological activities. Their distribution in biological systems is also different. A typical man weighing 70 kg contains about 90 g of sodium and 170 g of potassium as compared with only 5g of iron and 0.06 g of copper. *The most salient feature is that K^+ ions are present in higher concentrations inside the cells than Na^+ ions while their relative concentrations are reverse outside the cells.* In other words, K^+ ions are concentrated inside the cells while Na^+ ions are concentrated outside the cells. Sodium ions are primarily found in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into the cells. On the other hand, K^+ ions are most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and with Na^+ ions are responsible for the transmission of nerve signals. There is very considerable variation in the concentration of Na^+ and K^+ ions found on the opposite sides of cell membranes. For example, in blood plasma, Na^+ ions are present to the extent of 143 m mol L^{-1} while K^+ ions are present only upto 5 m mol L^{-1} within the red blood cells. However, these concentrations change to 10 m mol L^{-1} (Na^+) and 105 m mol L^{-1} (K^+) in the cell fluids. These ionic gradients control the development and the functioning of the nerve cells.

This has been explained in terms of a mechanism known as **sodium-potassium pump.** Because of large concentration gradient inside and outside the cells, the transport of Na^+ ion into the cell is favoured. Therefore, the Na^+ ions entering the cell must be pumped out again from the cell to maintain concentration gradients. The maintenance of these large concentration gradients provide a driving force to carry out important transport processes involving amino acids, sugars, nucleotides, etc. For this transport, some metabolic energy is expanded to maintain the concentration gradients of Na^+ and K^+ ions inside and outside the cells. This process is known as **sodium-potassium pump** which operates across the cell membrane. The energy for the transport of these ions is provided by the hydrolysis of energy rich molecules ATP. Thus, ***both sodium and potassium ions are essential ions for living organisms***.

The **Na^+ ions are** :

(*i*) major component of blood plasma.
(*ii*) important in transmission of nerve signals and function of heart.
(*iii*) important in activation of some enzymes.
(*iv*) important in regulating the flow of water across cell membranes.
(*v*) in transport of sugars and amino acids into cells.

The **K^+ ions** are required in the cells for

(*i*) activating many enzymes.
(*ii*) participating in the oxidation of glucose to produce energy rich ATP molecules.
(*iii*) proteins synthesis
(*iv*) participate with Na^+ ions in sodium – potassium pump for the transmission of nerve signals.

In general, more than 1/3 of the ATP is used by a resting animal and about 15 kg per 24 hr in a resting human for the operation of Na–K pump.

In 1957, Jens Skou discovered that membranes with sodium pump were found to contain an enzyme adenosin triphosphatase (ATPase), which is responsible for the action of sodium pump.

SOLVED EXAMPLES

❑ **Example 8.**

Why is that on being heated in excess supply of air, K, Rb, and Cs form superoxides in preference to oxides and peroxides ?

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Solution: K^+, Rb^+ and Cs^+ are large cations and superoxide ion, O_2^- is larger than oxide (O^{2-}) ion and peroxide (O_2^{2-}) ion. A larger cation can stabilize a large anion and therefore, these metals form superoxides in preference to oxides and peroxides.

❑ **Example 9.**

What happens when KO_2 reacts with water ? Write the balanced chemical equation for the reaction.

Solution: When KO_2 reacts with water an alkaline solution containing H_2O_2 is formed and oxygen gas is evolved.

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$
$$\text{or } 2O_2^- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$$

❑ **Example 10.**

Write balanced equations for reactions between :

(i) Na_2O_2 and water *(ii) KO_2 and water*

(iii) Na_2O and CO_2 **N.C.E.R.T.**

Solution:

(*i*) $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

(*ii*) $2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

(*iii*) $Na_2O + CO_2 \longrightarrow Na_2CO_3$.

Practice Problems

1. Among the alkali metals which element has
(*i*) highest melting point
(*ii*) most electropositive character
(*iii*) lowest size of ion
(*iv*) strongest reducing character

2. Out of LiOH, NaOH and KOH, which is the strongest base ?

3. Complete the following reactions :

(*i*) $Mg(NO_3)_2 \xrightarrow{\text{Heat}}$

(*ii*) $LiOH \xrightarrow{\text{Heat}}$

(*iii*) $Li + HC \equiv CH \longrightarrow$

(*iv*) $Na + O_2 \longrightarrow$

4. Can we store sodium in water or not ?

5. Lithium compounds are slightly covalent because of its greater ..... . Complete the statement.

6. What compounds are formed when Li, Na and K combine with oxygen ?

7. Which is most abundant metal among alkaline earth metal ?

8. Which is the most abundant element among alkali metal ?

9. Which among the alkali metals form nitride ?

10. Which of the following alkali metals is most electropositive ?
Li, Na, K, Rb or Cs.

Answers to Practice Problems

1. (*i*) Li (*ii*) Cs
(*iii*) Li (*iv*) Li

2. KOH

3. (*i*) $2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$
(*ii*) $2LiOH \longrightarrow Li_2O + H_2O$
(*iii*) $2Li + HC \equiv CH \longrightarrow LiC \equiv CLi + H_2$
(*iv*) $2Na + O_2 \longrightarrow Na_2O_2$

4. No, sodium can be stored in kerosene.

5. polarising power.

6. Li_2O, Na_2O_2, KO_2

7. Calcium.

8. Sodium

9. Lithium

10. Lithium

add on Conceptual Questions 1

Q. 1. Sodium metal is kept under kerosene. Explain.

Ans. Sodium metal is very reactive. When exposed to air, it reacts with oxygen, moisture and carbon dioxide present in the air.

$$4Na\,(s) \xrightarrow{O_2} \underset{\text{Sodium oxide}}{2Na_2O}$$

$$2Na_2O \xrightarrow{2H_2O} \underset{\text{Sod. hydroxide}}{4NaOH}$$

$$4NaOH \xrightarrow{2CO_2} \underset{\text{Sod. carbonate}}{2Na_2CO_3} + 2H_2O$$

Therefore, to prevent these reactions and protect the metal, sodium is kept under kerosene.

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CONCEPTUAL QA

Q. 2. LiCl is soluble in organic solvents. Explain

Ans. Li^+ has very high polarizing power and, therefore, LiCl is covalent in nature. Being covalent in nature, it is soluble in organic solvents.

Q. 3. Name the chief factors responsible for anomalous behaviour of lithium.

Ans. The anomalous behaviour of lithium is because of

(*i*) small size of atom and ion,

(*ii*) high ionization enthalpy, and

(*iii*) absence of *d*- orbitals in its valence shell.

Q. 4. Name the alkali metals which form superoxides when heated in excess of air.

Ans. Potassium, rubidium and cesium.

Q. 5. Name the metal which floats on water without any apparent reaction with it.

Ans. Lithium

Q. 6. Predict giving reason, the outcome of the reaction :

LiI + KF $\longrightarrow$

Ans. $LiI + KF \longrightarrow LiF + KI$

Large cation (K^+) can stabilize large anion (I^-).

Q. 7. Why does the following reaction :

$\geqslant C - Cl + MF \longrightarrow \geqslant C - F + MCl$

proceed better with KF than with NaF.

Ans. This is because the larger cation can stabilize larger anion.

Q.8. What compounds are formed when Li and Na combine with oxygen. Give the hydrolysis reactions of compounds formed. ***N.C.E.R.T.***

Ans. Li and Na combine with oxygen to form Li_2O and Na_2O_2. The hydrolysis reactions are :

$Li_2O + H_2O \longrightarrow 2LiOH$

$Na_2O_2 + H_2O \longrightarrow 2NaOH + H_2O_2$

Q. 9. Explain why sodium is less reactive than potassium. ***N.C.E.R.T.***

Ans. Potassium is more reactive than sodium because of its large size and low ionisation enthalpy in comparison to sodium.

Q. 10. Why are potassium and cesium, rather than lithium can be used in photoelectric cells ?

Ans. Potassium and cesium have low ionisation enthalpy values, so electrons can be easily ejected from these metals when light of suitable frequency strikes on their surfaces. Lithium has high ionization enthalpy and therefore, it does not show photoelectric effect and cannot be used in photoelectric cells.

Q. 11. Why are lithium salts commonly hydrated and those of other alkali ions usually anhydrous ?

Ans. Because of small size, Li^+ has high charge density and therefore, lithium salts are extensively hydrated.

Q. 12. Why is LiF almost insoluble in water whereas LiCl is soluble not only in water but is also in acetone? ***N.C.E.R.T.***

Ans. Both Li^+ and F^- have small size and therefore LiF has very high lattice enthalpy. Although hydration enthalpy of LiF is also high but it is less than lattice enthalpy (Lattice enthalpy of LiF = –1045 kJ, hydration enthalpy of LiF = –1034 kJ mol^{-1}). But LiCl has lower lattice enthalpy than corresponding hydration enthalpy and therefore, is soluble in water. LiCl has also some covalent character because of greater polarization hence it is also readily soluble in nonpolar solvents such as acetone.

Q. 13. Lithium is the only alkali metal to form nitride directly. Explain.

Ans. Li^+ being small in size can easily stabilize small nitride ion, N^{3-}. Other alkali metal ions of larger size cannot stabilize small nitride ion.

Q. 14. An aqueous solution of sodium carbonate gives alkaline tests. Why ? ***N.C.E.R.T.***

Ans. Sodium carbonate in aqueous solution gets hydrolysed to give OH^- ions and, therefore, gives alkaline tests.

$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$.

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Q. 15. Why is Li_2CO_3 decomposed at lower temperature whereas Na_2CO_3 at higher temperature ?

Ans. Li^+ ion being small in size, cannot stabilize large CO_3^{2-} ion therefore, Li_2CO_3 is unstable. On the other hand sodium is larger in size and can easily stabilize large CO_3^{2-} ions and form stable Na_2CO_3. This is because of lattice energy effects.

Q. 16. LiH, LiF and Li_3N show exceptional thermal stabilities. Explain.

Ans. Li^+ is small in size and has exceptionally high charge–radius ratio. Therefore, its salts with small anions such as F^-, H^- and N^{3-} are exceptionally stable due to their high lattice enthalpies.

CONCEPTUAL QA

Q. 17. Which out of Li or Na has greater value for the following properties :

(*i*) Hydration enthalpy **(*ii*) Stability of hydride**

(*iii*) Stability of carbonate **(*iv*) Basic character of hydroxide**

(*v*) Ionisation enthalpy.

Ans. (*i*) Li (*ii*) Li (*iii*) Na (*iv*) Na (*v*) Li

Q. 18. Which out of the following and why can be used to store an alkali metal ?

H_2O, C_2H_5OH, Benzene

Ans. Benzene can be used to store an alkali metal because other substances react with alkali metals as :

$$Na + H_2O \longrightarrow NaOH + \tfrac{1}{2}H_2$$

$$Na + C_2H_5OH \longrightarrow C_2H_5ONa + \tfrac{1}{2}H_2$$

Q. 19. Why are alkali metals not found free in nature ? ***N.C.E.R.T.***

Ans. Alkali metals are highly reactive and therefore, are not found free in nature. They are present in the combined state in the form of halides, oxides, silicates, borates, nitrates, etc.

Q.20. Why can cesium be used in photoelectric cell but lithium cannot?

Ans. Cesium has the lowest while lithium has the highest ionization enthalpy. Hence, cesium can lose electrons very easily and can be used in photoelectric cells.

Q.21. Complete the following reactions :

(*i*) $O_2^{2-} + H_2O \longrightarrow$ **(*ii*) $O_2^- + H_2O \longrightarrow$**

Ans. (*i*) $O_2^{2-} + 2H_2O \longrightarrow 2OH^- + H_2O_2$

(*ii*) $2O_2^- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$

Q.22. Can potassium carbonate like sodium carbonate be prepared by Solvay process ? Explain.

Ans. Potassium carbonate cannot be prepared by the Solvay-ammonia process like sodium carbonate. This is because unlike $NaHCO_3$ which is sparingly soluble in water, $KHCO_3$ is fairly soluble in water. When CO_2 is passed through ammoniated brine, $NaHCO_3$ gets precipitated but $KHCO_3$ does not get precipitated when CO_2 is passed through an ammoniated solution of potassium chloride. Therefore, K_2CO_3 cannot be prepared by the Solvay ammonia process.

CHEMISTRY OF ALKALINE EARTH METALS

The group 2 of the periodic table consists of the elements *beryllium* (Be), *magnesium* (Mg), *calcium* (Ca), *strontium* (Sr), *barium* (Ba) and *radium* (Ra). These elements are known as **alkaline earth metals.**

OCCURRENCE

Magnesium like its heavier congeners occurs in crustal rocks mainly as insoluble carbonates, sulphates and silicates. It also occurs to about 0.13 % in sea water as chloride and sulphate. Magnesium is **sixth** most abundant element following calcium. It occurs as **dolomites** ($MgCO_3.CaCO_3$), **magnesites** ($MgCO_3$), **epsomite** ($MgSO_4.7H_2O$). As silicates it is represented by common basaltic mineral olivine [$(MgFe)_2SiO_4$] and by soapstone (talc) [$Mg_3Si_4O_{10}(OH)_2$], etc. Calcium is fifth most abundant element in earth's crust. It is found in vast sedimentary rocks of $CaCO_3$ existing as whole mountain ranges of **limestone, marble** and **chalk**. Other important minerals are gypsum ($CaSO_4.2H_2O$), anhydrite $CaSO_4$, fluorite (CaF_2) and fluoroapatite [$3Ca_3(PO_4)_2.CaF_2$].

Strontium occurs as **celestite** ($SrSO_4$) and **strontianite** ($SrCO_3$). The main ore of barium is baryte ($BaSO_4$). It also occurs as witherite ($BaCO_3$). Beryllium is less abundant like Li. It is found as surface deposits of beryl in pegmatite rocks. Radium occurs only in association with uranium having terrestrial abundance of approximately 10^{-6} ppm.

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GENERAL CHARACTERISTICS OF ALKALINE EARTH METALS

The general relationships throughout the group are similar to those in Group 1. Table 5 and 6 give the electronic configurations and atomic and physical properties of Group 2 elements and these are discussed below :

Electronic Configurations and Atomic Properties

1. Electronic Configurations. These elements are called **alkaline earth metals.** The atoms of these elements have two electrons in their valence shell preceded by the noble gas configuration. Their general configuration may be written as **[Noble gas] ns^2** where n represents the valence shell (Table 5).

2. Atomic and ionic sizes. *The atomic and ionic radii of the members of the family are smaller than the corresponding members of the alkali metals.*

Explanation. The alkaline earth metals have a higher nuclear charge and therefore, the electrons are attracted more towards the nucleus. As a result, their atomic and ionic radii are smaller than those of alkali metals. On moving down the group, the radii increase due to gradual increase in the number of the shells and the screening effect.

3. Ionisation enthalpy. The alkaline earth metals *have low ionisation enthalpies due to fairly large size of the atoms.* Since the atomic size increases down the group, the ionisation enthalpy decreases (Table 5). A comparison of the ionisation enthalpies of the members of groups 1 and 2 shows that the members present in the second group have higher values as compared to those of group 1 because they have smaller size and electrons are more attracted towards the nucleus of the atoms.

It may be noted that *although IE_1 values of alkaline earth metals are higher than those of alkali metals, but the IE_2 values of alkaline earth metals are much smaller than those of alkali metals.* The ionisation enthalpy values of sodium (alkali metal) and magnesium (alkaline earth metal) are given below :

Element	IE_1	IE_2
Na	496 kJ mol^{-1}	4562 kJ mol^{-1}
Mg	737 kJ mol^{-1}	1450 kJ mol^{-1}

Table 5. The electronic configuration of alkaline earth metals.

Element	Symbol	Atomic No.	Electronic Configuration
Beryllium	Be	4	[He]$2s^2$
Magnesium	Mg	12	[Ne]$3s^2$
Calcium	Ca	20	[Ar]$4s^2$
Strontium	Sr	38	[Kr]$5s^2$
Barium	Ba	56	[Xe]$6s^2$
Radium	Ra	88	[Rn]$7s^2$

Table 6. Physical constants of alkaline earth metals.

	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Atomic radius (pm)	112	160	197	215	222	—
Ionic radius M^{2+} (pm)	31	72	100	118	135	148
Density (g cm^{-3})	1.84	1.74	1.55	2.63	3.59	(5.5)
Ionisation enthalpy (kJ mol^{-1})						
IE_1	899	737	590	549	503	509
IE_2	1757	1450	1146	1064	965	979
Electronegativity	1.57	1.31	1.00	0.95	0.89	0.90
Melting point (K)	1560	924	1124	1062	1002	973
Boiling point (K)	2745	1363	1767	1655	2078	(1973)
Hydration enthalpy (kJ mol^{-1})	−2494	−1921	−1577	−1443	−1305	—
$E°$ (V) $M^{2+}\|M$	−1.97	−2.36	−2.84	−2.89	−2.92	−2.92
Occurrence in lithosphere (ppm)	2*	27640*	46600*	384	390	10^{-6}

Values in brackets represent uncertain values

* These are expressed as 2.76 (Mg) and 4.66% (Ca) by wt. respectively.

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Explanation. In case of alkali metals (*i.e.*, Na) the second electron is to be removed from a cation which has already acquired a noble gas configuration. On the other hand, in the alkaline earth metals (*i.e.*, Mg), the second electron is to be removed from a monovalent cation, $Mg^+ : (1s^2 2s^2 2p^6 3s^1)$ which still has one electron in the outermost shell. Thus, the second electron in Mg can be removed easily.

$$\underset{1s^2 2s^2 2p^6 3s^1}{Na(g)} \xrightarrow[-e^-]{IE_1} \underset{1s^2 2s^2 2p^6}{Na^+(g)} \xrightarrow[-e^-]{IE_2} \underset{1s^2 2s^2 2p^5}{Na^{2+}(g)}$$

Stable configuration

$$\underset{1s^2 2s^2 2p^6 3s^2}{Mg(g)} \xrightarrow[-e^-]{IE_1} \underset{1s^2 2s^2 2p^6 3s^1}{Mg^+(g)} \xrightarrow[-e^-]{IE_2} \underset{1s^2 2s^2 2p^6}{Mg^{2+}(g)}$$

Not very stable

Thc IE_3 of Mg will bc vcry high bccausc thc electron is to be removed from stable noble gas configuration.

4. Hydration enthalpy. *The hydration enthalpies of alkaline earth metal ions are larger than those of the corresponding alkali metal ions.* This is due to smaller size of alkaline earth metal ions as compared to corresponding alkali metal ions of the same period. Due to smaller size, the alkaline earth metal ions are strongly attracted by polar water molecules and hence have larger hydration enthalpies. Thus, the compounds of alkaline earth metals are more extensively hydrated than those of alkali metals. For example, $MgCl_2$ and $CaCl_2$ exist as $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$ while NaCl and KCl donot form such hydrates. The number of molecules of water of crystallisation decreases as the ions become larger. For example, $BaCl_2$ exists as $BaCl_2.2H_2O$.

Like alkali metals ions, *the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.*

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

This decrease in hydration enthalpies down the group is due to increase in ionic size of the ion.

Physical Properties

1. Physical appearance. The alkaline earth metals, in general are silvery white, lustrous and relatively soft. However, these are harder than the corresponding alkali metals. Beryllium and magnesium appear to be somewhat greyish.

2. Melting and boiling points. *Alkaline earth metals have low melting and boiling points which are higher than the corresponding alkali metals in the same period due to comparatively smaller size.* However, melting and boiling points do not show regular trends.

Explanation. The atoms of alkaline earth metals have smaller size as compared to alkali metals. Therefore, they are more closely packed in their crystal lattices and hence, they have higher melting and boiling points.

3. Electropositive and metallic character. Because of the low ionisation enthalpies of alkaline earth metals, they are strongly electropositive in nature. However, *these are not as strongly electropositive as the alkali metals of group 1 because of comparatively higher ionisation enthalpies.* The electropositive character **increases down the group** *i.e.,* from Be to Ba.

4. Characteristic flame colouration. Except for Be and Mg, the alkaline earth metal salts impart characteristic colours to the flame.

Be	Mg	Ca	Sr	Ba	Ra
—	—	Brick red	Crimson red	Grassy green	Crimson red

Beryllium and magnesium do not give any characteristic flame colours.

Explanation. The alkaline earth metals give characteristic flame colours because their ionisation enthalpies are low. Therefore, the valence electrons in these atoms can be easily excited to higher energy states by the energy of flame of bunsen burner. When these excited electrons (excited state is unstable state) come back to ground state they emit radiations which fall in the visible region. Therefore, they give colours to the flame. On the other hand, *beryllium and magnesium atoms are comparatively smaller and their ionisation enthalpies are very high. Hence, the energy of the flame is not sufficient to excite their electrons to higher energy levels. These elements, therefore, do not give any colour in Bunsen flame.*

The flame test for calcium, strontium and barium is helpful in their detection in qualitative analysis.

5. Electrical and thermal conductivities. The alkaline earth metals have high electrical and thermal conductivities which are typical characteristics of metals.

6. Tendency to form bivalent ions. The alkaline earth metals exhibit a valency of +2 as they can lose two electrons and form bivalent ions. Inspection of Table 5 reveals that the second ionisation enthalpy (IE_2) of alkaline earth metals is greater than the first ionisation enthalpy (IE_1). It, thus appears that if ionisation enthalpy is the only factor involved in the formation of divalent ions, we would expect *that alkaline earth metals would prefer to form +1 ions (E^+) rather than + 2 ions (E^{2+}).* Actually, they predominatly show +2 valency, *e.g.*, Mg^{2+}, Ca^{2+}, Ba^{2+}, etc.

Explanation. This can be explained as :

(*i*) Divalent ions have the stable noble gas configuration.

(*ii*) In solution, the divalent ions of alkaline earth metals are extensively hydrated and the high hydration energies of E^{2+} ions make them more stable than E^+ ions. It is observed that the amount of energy released

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when E^{2+} ion is dissolved in water is much more that that for E^+ ion. *This large amount of extra energy released in the hydration of + 2 ions compensates the second ionisation enthalpy required for the formation of such ions.*

(*iii*) In the solid state, the divalent cations form stronger lattices than monovalent cations and therefore, a lot of energy called *lattice enthalpy* is released. *It is the greater lattice enthalpy of E^{2+} ion which compensates for the high second ionisation enthalpy and is responsible for its greater stability as compared to E^+ ion.*

This can be easily understood by considering the overall energy changes for the formation of MgCl and $MgCl_2$ in water with the help of Born Haber cycle. The various steps are :

$$Mg(s) \longrightarrow Mg(g) \qquad \Delta H_{sublimation} = 150 \text{ kJ mol}^{-1}$$

$$Mg(g) \longrightarrow Mg(g) + e^- \qquad \Delta H_{I.E.} = 737 \text{ kJ mol}^{-1}$$

$$\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g) \qquad \Delta H_{atomisation} = 122 \text{ kJ mol}^{-1}$$

$$Cl(g) \longrightarrow Cl^-(g) \qquad \Delta H_{eg} = -348 \text{ kJ mol}^{-1}$$

$$Mg^+(g) + Cl^-(g) + nH_2O \longrightarrow Mg^+(aq) + Cl^-(aq) \qquad \Delta H_{hydration} = -735 \text{ kJ mol}^{-1}$$

Net energy change = –74 kJ mol^{-1}

$$Mg(s) \longrightarrow Mg(g) \qquad \Delta H_{sublimation} = 150 \text{ kJ mol}^{-1}$$

$$Mg(g) \longrightarrow Mg^{2+} + 2e^- \qquad \Delta H_{I.E.} = 2188 \text{ kJ mol}^{-1}$$

$$Cl_2(g) \longrightarrow 2Cl \qquad \Delta H_{atomisation} = 2 \times 122 \text{ kJ mol}^{-1}$$

$$2Cl + 2e^- \longrightarrow 2Cl^- \qquad \Delta H_{eg} = -2 \times 348 \text{ kJ mol}^{-1}$$

$$Mg^{2+}(g) + 2Cl^-(g) + nH_2O \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq) \qquad \Delta H = -2670 \text{ kJ mol}^{-1}$$

Net energy change = –784 kJ mol^{-1}

Thus, it is clear that during the formation of $MgCl_2$ in water, more energy is released and therefore, it is more readily formed.

Similary, it can be shown that net energy change for the formation of $MgCl_2(s)$ is –642 kJ mol^{-1} and that for the formation of MgCl(*s*) is –125 kJ mol^{-1}. This shows that *$MgCl_2(s)$ is more stable as compared to MgCl(s)*

Thus, the alkaline earth metals prefer to form divalent ions rather than monovalent ions.

Chemical properties

Because of their *low ionisation enthalpies* and *high electropositive character*, the alkaline earth metals have strong tendency to lose valence electrons. Therefore, they are very reactive. The reactivity of these elements **increases** on going down the group. However, alkaline earth metals are *in general less reactive than alkali metals.* The chemistry is mainly dominated by the dipositive oxidation state (E^{2+}). Some of the general trends are discussed below :

1. Reactivity towards air or oxygen.

The alkaline earth metals being less electropositive than alkali metals, react with air or oxygen slowly upon heating to form oxides, MO. **Beryllium and magnesium are kinetically inert towards oxygen because of the formation of a film of oxide on their surface.** However, powdered beryllium burns brilliantly on ignition to give BeO and Be_3N_2.

$$2Be + O_2 \xrightarrow{\text{Heat}} 2BeO$$

air — Beryllium oxide

$$3Be + N_2 \xrightarrow{\text{Heat}} Be_3N_2$$

from air — Beryllium nitride

Magnesium is more electropositive and burns with dazzling brilliance in air to give a mixture of MgO and Mg_3N_2.

$$4Mg + \text{air } (O_2, N_2) \xrightarrow{\text{Heat}} MgO + Mg_3N_2$$

Calcium, strontium and barium are readily attacked by air to form oxide and nitride.

Thus, the reactivity with oxygen **increases** *as we move down the group due to increasing electropositive character of the elements.* Therefore, calcium, barium and strontium are stored in paraffin but beryllium and magnesium are not stored in paraffin because they form a protective layer of oxide on their surface .

2. Reactivity towards hydrogen.

All the elements except beryllium combine with hydrogen upon heating to form ionic hydrides, MH_2.

$$Ca + H_2 \xrightarrow{\text{Heat}} CaH_2$$

Calcium hydride

BeH_2, however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.

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$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3.$$

Both BeH_2 and MgH_2 are covalent compounds having polymeric structures. MgH_2 is covalent while all other hydrides are ionic.

Calcium hydride is known as **hydrolith.**

The hydrides are highly reactive towards water and form hydroxides and liberate hydrogen.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

3. Reactivity towards water.

The alkaline earth metals have lesser tendency to react with water as compared to alkali metals. They combine with water slowly to form hydroxides. Beryllium and magnesium are kinetically inert to water. Beryllium does not react with water or steam even at red heat.

Calcium, stronium and barium react with water with less difficulty.

$$Ca + 2H_2O \xrightarrow{Heat} Ca(OH)_2 + H_2$$

Like alkali metals, the hydroxides are basic in nature and basic strength increases down the family.

Lattice enthalpy versus hydration enthalpy

The solubility of a salt in water depends upon two factors :

(*i*) lattice enthalpy

(*ii*) hydration enthalpy.

Lattice enthalpy *is the amount of* **energy required** *to break one mole of a solid salt into its ions as :*

$$MX(s) \xrightarrow{\text{Lattice enthalpy}} M^+(g) + X^-(g)$$

Greater the lattice enthalpy, more will be the energy required to break the lattice.

Hydration enthalpy *is the amount of* **energy released** *when one mole of a solid salt gets dissolved in water (hydrated).* Therefore, the net effect will be the energy of solution.

Net enthalpy = Lattice enthalpy – Hydration enthalpy.

Now we know that for the feasibility of a process *i.e.*, solubility of the salt, the net energy change should be negative *i.e.*, energy should be released. Thus, it becomes clear that

- *if hydration enthalpy is* **more** *than lattice enthalpy; salt will* **dissolve**
- *if hydration enthalpy is* **less** *than lattice enthalpy; salt will* **not dissolve.**

This can easily explain the increasing solubility of alkaline earth metal hydroxides on moving down the group. The lattice enthalpy decreases with increase in size of the cation and therefore, solubility increases from Be to Ba.

This can also explain easily as to why alkali metal salt, say Na_2SO_4 is soluble in water whereas alkaline earth metal salt, $BaSO_4$ is insoluble. The lattice enthalpy of Na_2SO_4 is less than the hydration enthalpy whereas the lattice enthalpy of $BaSO_4$ (because of bivalent charge) is very high so that hydration enthalpy released is not sufficient to break the lattice and it remains insoluble.

4. Action with acids.

Alkaline earth metals react with acids and liberate hydrogen. However, Be reacts slowly because it is rendered passive by concentrated HNO_3. This is because conc. HNO_3 is a strong oxidizing agent and it forms a very thin layer of oxide on the surface of the metal, which protects it from further attack by acid.

$$M + 2HCl \longrightarrow MCl_2 + H_2$$

(M = Be, Mg, Ca, Sr, Ba)

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

Be is amphoteric because it also reacts with NaOH giving H_2 and sodium berrylate.

$$Be + 2NaOH + 2H_2O \longrightarrow Na_2[Be(OH)_4] + H_2$$

or $NaBeO_2 . 2H_2O + H_2$

Sodium beryllate

Mg, Ca, Sr and Ba do not react with NaOH and are purely basic. This shows that basic properties increase on descending the group.

5. Reactivity towards halogens.

All the alkaline earth metals combine with halogens at higher temperatures forming their halides.

$$M + X_2 \longrightarrow MX_2 \quad (X = F, Cl, Br, I)$$

The metal halides can also be obtained by the action of halogen acids on metals, their oxides, carbonates and hydroxides.

$$MO + 2HX \longrightarrow MX_2 + H_2O$$

$$M(OH)_2 + 2HX \longrightarrow MX_2 + 2H_2O$$

BeF_2 is conveniently prepared by thermal decomposition of $(NH_4)_2BeF_4$ while $BeCl_2$ can be made from the oxide as :

$$BeO + 2NH_3 + 4HF \longrightarrow (NH_4)_2[BeF_4] \xrightarrow{Heat} BeF_2 + 2NH_4F$$

$$BeO + C + Cl_2 \xrightleftharpoons{870 - 1070K} BeCl_2 + CO$$

Beryllium chloride can also be prepared by heating beryllium oxide with carbon tetrachloride.

$$2BeO + CCl_4 \xrightarrow{973\ K} 2BeCl_2 + CO_2$$

6. Reactivity with ammonia.

Like alkali metals, alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.

$$M + (x + y)\,NH_3 \longrightarrow M(NH_3)_x^{2+} + 2e^-(NH_3)_y$$

From these solutions, the ammoniates of the general formula $[M(NH_3)_6]^{2+}$ may be recovered.

7. Tendency to form complexes.

The group 2 elements have tendency to form some stable complexes. Among these, beryllium and

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magnesium have maximum tendency to form complexes. This is due to their small size and higher charge density. For example, beryllium forms complexes of the type $[BeF_4]^{2-}$

$$BeF_2 + 2F^- \longrightarrow [BeF_4]^{2-}$$

Chlorophyll is an important complex of magnesium.

8. Reducing power.

Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials (Table 4). Beryllium has less negative value as compared to other alkaline earth metals. However, its reducing nature is due to large hydration enthalpy associated with the small size of Be^{2+} ion and relatively large value of the enthalpy of atomization of the metal. Magnesium cation is more easily reduced than the other heavier cations of the group because its small size leads to a relatively large negative value for its hydration enthalpy.

GENERAL CHARACTERISTICS OF COMPOUNDS OF ALKALINE EARTH METALS

The alkaline earth metals form compounds having dipositive ions, MX_2. Due to the increased nuclear charge and smaller ionic size, the alkaline earth metals are expected to form less ionic compounds than the corresponding alkali metals. The tendency to form ionic compounds increases as we move down the group. For example, the oxides and other compounds of Be and Mg are more covalent than those formed by the heavier and the large sized members (Ca, Sr, Ba).

The general characteristics of some compounds of alkaline earth metals are discussed below :

1. Oxides and hydroxides

All the alkaline earth metals form oxides of the formula MO (M is alkaline earth metal). These can be prepared by reacting the metal with oxygen :

$$2M + O_2 \xrightarrow{\text{Heat}} \underset{\text{(Monoxide)}}{2MO} \quad (M = Be, Mg, Ca)$$

These monoxides can be best prepared by the calcination of their carbonates.

$$MCO_3 \longrightarrow MO + CO_2$$

(M = Be, Mg, Ca, Sr or Ba)

The decomposition temperatures for these carbonates are :

	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Decomposition temperature	523 K	813 K	1173 K	1562 K	1633 K

All these alkaline earth metal oxides except BeO have rock salt (NaCl type) structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are very high and therefore, they are very stable.

Metal oxide	BeO	MgO	CaO	SrO	BaO
$\Delta_f H^\ominus$ (kJ mol^{-1})	550	590	623	590	545

Among the oxides, *BeO is amphoteric while oxides of other elements are basic in nature.*

BeO	MgO	CaO, SrO, BaO
Amphoteric	Weakly basic	Basic

The amphoteric character of BeO is supported by the fact that it reacts with acids as well as alkalies.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O \quad \text{(Basic nature)}$$

$$BeO + 2NaOH \longrightarrow \underset{\text{Sod. beryllate}}{Na_2BeO_2} + H_2O \quad \text{(Acidic nature)}$$

The decrease in basic character of oxides from Be to Ba is because of decrease in polarizing power with increase in ionic size.

The oxides of Be and Mg (BeO, MgO) are almost insoluble in water while the oxides of rest of the metals dissolve in water to from hydroxides.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + \text{Heat}$$

The insolubility of BeO and MgO in water is due to their large lattice enthalpies.

All these oxides except BeO react with water to form sparingly soluble hydroxides :

$$MO + H_2O \longrightarrow M(OH)_2$$

The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$.

The basic character of hydroxides is due to the low ionisation enthalpies of these metals. Because of low ionisation enthalpies, the M—O bond in MOH is weak and it can cleave to give OH^- ions in solution. Since, the ionisation enthalpy decreases down the family, therefore, the basic strength of the hydroxides increases. For example, $Be(OH)_2$ is amphoteric, $Mg(OH)_2$ is mildly basic while others are strong bases.

Beryllium hydroxide is amphoteric in nature because it reacts with acids as well as alkalies.

$$Be(OH)_2 + 2HCl + 2H_2O \longrightarrow [Be(OH)_4]Cl_2$$

$$Be(OH)_2 + 2OH^- \longrightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$$

Hydroxides of Alkali and Alkaline earth metals

LiOH	$Be(OH)_2$ Amphoteric
NaOH	$Mg(OH)_2$ Mild base
KOH	$Ca(OH)_2$ Strong base
RbOH	$Sr(OH)_2$ Strong base
CsOH	$Ba(OH)_2$ Very strong base

BASIC CHARACTER INCREASES

All alkali metal hydroxides are strong bases

BASIC CHARACTER DECREASES

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The hydroxides of alkaline earth metals are less basic than alkali metals of the corresponding periods. The lesser basic strength of hydroxides of alkaline earth metal hydroxides is due to their

(*i*) *high ionisation enthalpies*

(*ii*) *small ionic size and*

(*iii*) *dipositive charge on the ions.*

As a result, the M—O bond in these hydroxides is relatively stronger than that of corresponding alkali metals and therefore, does not break. Therfore, they are less basic than corresponding alkali metals.

The hydroxides of alkaline earth metals are less soluble than alkali metal hydroxides. However, the solubility of hydroxides in water increases with increase in size of the metal. $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble, $Ca(OH)_2$ is sparingly soluble while $Sr(OH)_2$ and $Ba(OH)_2$ are fairly soluble. This trend is due to increase in size of the cation on moving down the group so that their lattice enthalpies decrease. Due to decrease in lattice enthalpies, the hydration enthalpies become more and more and the solubility of hydroxides in water increases.

2. Halides

The halides of alkaline earth metals can be obtained either by directly reacting with halogens or by the action of halogen acids on metals, their oxides, carbonates or hydroxides.

$$M + X_2 \longrightarrow MX_2 \qquad (X = Cl_2, Br_2)$$

$$MO + 2HX \longrightarrow MX_2 + H_2O$$

$$M(OH)_2 + 2HX \longrightarrow MX_2 + 2H_2O$$

The important **characteristics** of halides of alkaline earth metals are :

(*i*) Beryllium halides are covalent while all other halides are ionic and are readily soluble in water.

(*ii*) $BeCl_2$ is relatively low melting solid and volatile while others have high melting points. $BaCl_2$ has very high melting point.

(*iii*) Being covalent $BeCl_2$ is soluble in organic solvents. Of the other halides $MgBr_2$ and MgI_2 are soluble in organic solvents.

(*iv*) The anhydrous halides of alkaline earth metals are **hygroscopic** *i.e.*, they absorb water molecules and form hydrates such as $BeCl_2 . 4H_2O$, $MgCl_2 . 6H_2O$, $CaCl_2 . 6H_2O$. The tendency to form halide hydrates gradually decreases down the group *e.g.*, $MgCl_2.8H_2O$, $CaCl_2 . 6H_2O$, $SrCl_2 . 8H_2O$ and $BaCl_2 . 2H_2O$. Because of this property, anhydrous calcium chloride is used as a *dehydrating agent*. $BeCl_2$ gets hydrolysed by moisture and, therefore, gives fumes of hydrochloric acid.

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

The hydrated chlorides, bromides and iodides can be dehydrated by heating but those of magnesium and beryllium get hydrolysed.

(*v*) The fluorides of alkaline earth metals are sparingly soluble in water. The solubility increases slightly with increase in cation size.

(*vi*) Except for $BeCl_2$ and $MgCl_2$, the chlorides of the other members impart characteristic flame colours.

$CaCl_2$	$SrCl_2$	$BaCl_2$
Brick red	Crimson	Grassy green

Be and Mg chlorides do not give flame colourations because of their high ionisation enthalpies. The energy of bunsen flame is not sufficient to excite the outermost electron in Be and Mg (already discussed). Of all the fluorides of alkaline earth metals, CaF_2 is very important because fluorspar (CaF_2) is the only large scale source of fluorine.

Beryllium chloride.

It is prepared by heating beryllium oxide with chlorine vapours in the presence of carbon.

$$BeO + Cl_2 + C \xrightarrow{870\text{-}1070\ K} BeCl_2 + CO$$

$BeCl_2$ can also be prepared by direct high temperature chlorination of metallic beryllium or Be_2C.

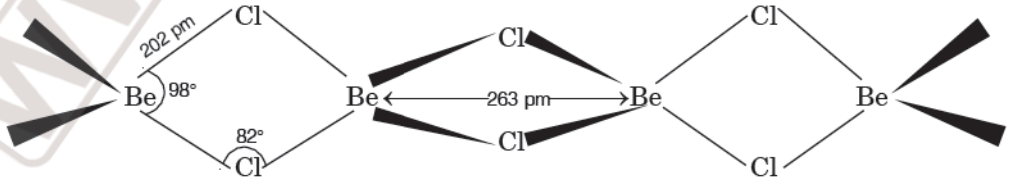

Fig. 5. Polymeric structure of $BeCl_2$.

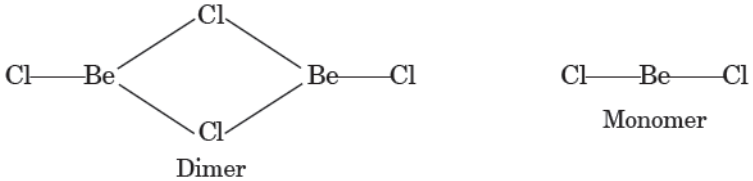

Fig. 6 Dimer (vapour phase) and monomer of $BeCl_2$.

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Structure of $BeCl_2$. In the solid state, beryllium chloride has a **polymeric chain structure** as shown in Fig. 5.

In this case, each Be atom is terahedrally surrounded by four Cl atoms. Two of the chlorine atoms are bonded by covalent bonds while the other two by coordinate bonds. The polymeric structure of $BeCl_2$ is due to its electron deficient nature. It has only four electrons in the valence shell and can accept two electron pairs (from neighbouring Cl atoms forming coordinate bonds) to complete its octet.

In the vapour phase, $BeCl_2$ exists as **dimer** (Fig. 6) which dissociates into the **linear monomer** at 1200 K.

3. Salts of oxo acids

Alkaline earth metals also form salts of oxoacids. Some of these are :

(*a*) Carbonates. The carbonates of alkaline earth metals can be prepared by passing carbon dioxide in limited supply through the solutions of their hydroxides.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

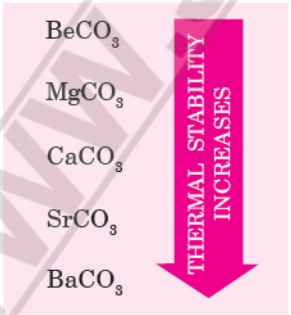
The alkaline earth metal carbonates being insoluble in water can be precipitated by the addition of a sodium or ammonium carbonate solution to a solution of soluble salt of these metals.

Most beryllium salts of strong oxoacids crystallize as soluble hydrates. Beryllium carbonate is very prone to hydrolysis and can be precipitated only in the atmosphere of carbon dioxide.

All carbonates decompose on heating to give carbon dioxide and metal oxide.

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

The stability of these carbonates increases down the group. For example, *$BeCO_3$ is least stable while $BaCO_3$ is the most stable.* **The solubilities of the metal carbonates in water decreases down the family.** For example, $BeCO_3$ is slightly soluble in water while $BaCO_3$ is completely insoluble.



However, all these carbonates become more soluble in the presence of carbon dioxide in water due to the formation of bicarbonate ion (HCO_3^-). But bicarbonates have not been isolated in the pure state.

(*b*) Sulphates. The sulphates of alkaline earth metals are all white solids and stable to heat. These can be formed by the action of dil H_2SO_4 on metals, metal oxides, metal hydroxides or metal carbonates.

$$Ca + H_2SO_4 \longrightarrow CaSO_4 + H_2$$
$$CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$$

Beryllium, magnesium and calcium sulphates crystallize in hydrated form as : $BeSO_4.4H_2O$, $MgSO_4.7H_2O$, $CaSO_4.2H_2O$. The sulphates of strontium and barium crystallize without water.

The sulphates of alkaline earth metals are less soluble than the corresponding salts of alkali metals. $BeSO_4$ and $MgSO_4$ are readily soluble, and their solubilities decrease on going down the group. This *is due to higher lattice enthalpies of alkaline earth metal sulphates than alkali metal sulphates* (as already explained). On moving down the group, the hydration enthalpy decreases with increase in size of the metal ion and consequently their solubilities decrease. The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore, their sulphates are soluble.

(*c*) Oxalates. The oxalates of Ca, Sr and Ba are sparingly soluble and solubility increases from Ca to Ba. Beryllium oxalate is highly soluble.

(*d*) Nitrates. The alkaline earth metals form nitrates by dissolution of carbonates in dilute HNO_3. Magnesium nitrate crystallizes with six water molecules ($MgNO_3.6H_2O$) while barium nitrate crystallizes as anhydrous salt. All these nitrates decompose on heating to give oxide.

$$2M(NO_3)_2 \xrightarrow{\text{Heat}} 2MO + 4NO_2 + O_2$$
(M = Be, Mg, Ca, Sr, Ba)

Strontium and barium nitrates are used in pyrotechnics for giving red and green flames.

Sparingly soluble salts		Soluble salts
MSO_4 and MCO_3	$M(OH)_2$	$M(NO_3)_2$
Mg, Ca, Sr, Ba (Decreases) decrease in solubility is due to decrease in hydration enthalpy.	Mg, Ca, Sr, Ba (Increases) increase in solubility is due to decrease in lattice enthalpy.	Mg, Ca (Increase); Sr, Ba (Decrease)

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Solubility and thermal stability of oxo salts

As already studied the solubility of salts depends upon two factors :

(*i*) Lattice enthalpy of the salt to break into ions.

(*ii*) Hydration enthalpy released when ions are hydrated.

The carbonates and sulphates of alkaline earth metals are less soluble than corresponding alkali metal salts. Their solubility decreases down the group due to decrease in the hydration enthalpy. For example, $MgCO_3$ is slightly soluble in water whereas $BaCO_3$ is almost insoluble. Similarly, magnesium sulphate is soluble in water, calcium sulphate is slightly soluble while $SrSO_4$ and $BaSO_4$ are insoluble.

Among the hydroxides there is increase in solubility as we go down the group. This is due to decrease in the lattice enthalpy. However, alkaline earth metal nitrates do not show regular order. The solubility increases from Mg to Ca and then decreases from Sr to Ba.

Thermal stability of the salts depend upon their lattice enthalpy. It depends upon two factors :

(*i*) The smaller the ions, the more closely they can approach in the lattice and the higher is the lattice enthalpy.

(*ii*) The greater the charges on the ions, the larger is the attraction between them and higher is the lattice enthalpy.

For example, the carbonates of alkaline earth metals are relatively less stable towards heat and decompose to CO_2. However, their stability increases as we move down the group. The temperatures at which these carbonates decompose are

$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
< 373 K	813 K	1173 K	1563 K	1635 K

Thermal stability increases

Nitrates and hydroxides also decompose to corresponding oxides. The O^{2-} ion is more highly charged than the NO_3^- and OH^-. Therefore, $E^{2+}O^{2-}$ have high lattice enthalpies than nitrates and hydroxides.

$$2Mg(NO_3)_2(s) \longrightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$$

$$Mg(OH)_2(s) \longrightarrow MgO(s) + H_2O(l)$$

DIFFERENCES BETWEEN BERYLLIUM AND MAGNESIUM

Beryllium, the first member of the alkaline earth metals family shows **anomalous** behaviour as compared to magnesium and the rest of the members.

It is mainly because of the following reasons :

(i) small size of the atom or its ion

(ii) high ionisation enthalpy and electronegativity

(iii) absence of d-orbitals.

Some of the **important differences** between beryllium and magnesium are given below :

(*i*) Beryllium is harder than magnesium.

(*ii*) It possesses higher boiling and melting points as compared to magnesium.

(*iii*) Beryllium does not react with water even at elevated temperatures. On the other hand, magnesium reacts with boiling water.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

(*iv*) Beryllium does not combine with hydrogen directly to form hydride whereas magnesium does.

(*v*) Because of high ionisation enthalpy and small size, beryllium forms covalent compounds while magnesium forms ionic compounds. Because of covalent character, salts of beryllium are easily hydrolysed. For example,

$$BeCO_3 + 4H_2O \longrightarrow [Be(H_2O)]^{2+} + CO_3^{2-}$$

(*vi*) Beryllium does not exhibit coordination number more than four because its valence shell has only four orbitals. The other members of the group can have coordination number of six by making use of *d*–orbitals. Beryllium carbide with water gives methane while magnesium carbide gives acetylene.

$$Be_2C + 2H_2O \longrightarrow 2BeO + \underset{\text{Methane}}{CH_4}$$

$$MgC_2 + 2H_2O \longrightarrow Mg(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

(*vii*) The oxide and hydroxide of beryllium are amphoteric while those of other elements in the group are basic.

DIAGONAL SIMILARITIES OF BERYLLIUM AND ALUMINIUM

Beryllium shows some similarities with aluminium due to *diagonal relationship*. Some common examples are :

(*i*) Both Be and Al have same electronegativity values (Be = 1.5, Al = 1.5) and their charge/radius ratios (Be = 0.064 and Al = 0.060) are similar indicating similar field strengths.

(*ii*) Both Be and Al form covalent compounds.

(*iii*) Beryllium and aluminium are resistant to the action of acids due to the formation of a protective film of oxide on the surface.

(*iv*) Both form soluble complexes by action of alkalies such as beryllates $[Be(OH)_4]^{2-}$ and aluminates $[Al(OH)_4]^-$.

(*v*) BeO and Al_2O_3 are amphoteric *i.e.*, they dissolve in acids as well as in bases.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH \longrightarrow \underset{\text{Sod. beryllate}}{Na_2BeO_2} + H_2O$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow \underset{\text{Sodium meta-aluminate}}{2NaAlO_2} + H_2O$$

(*vi*) The carbides of both B and Al liberate methane with water.

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$$

$$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4$$

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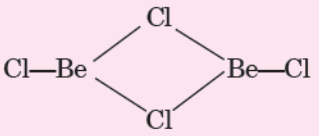
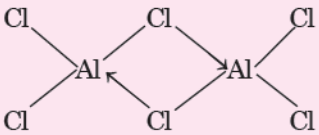
(*vii*) Both the metals are weakly electropositive in nature.

(*viii*) Beryllium and aluminium have strong tendency to form complexes. They form fluoro complex anions, BeF_4^{2-} and AlF_6^{3-} in solution. The other group 2 metals do not form stable fluoro complexes in solution.

(*ix*) Beryllium dissolves in alkalies to give beryllate ion $[Be(OH)_4]^{2-}$ while aluminium dissolves to give $[Al(OH)_6]^{3-}$.

(*x*) $BeCl_2$ like Al_2Cl_6 has a bridged polymeric structure in vapour phase as shown below.





Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.

(*xi*) Salts of these metals form hydrated ions *e.g.*, $[Be(H_2O)_4]^{2+}$ and $[Al(H_2O)_6]^{3+}$ in aqueous solutions.

(*xii*) Because of similarity in charge/size ratios both have strong tendency to form complexes. For example, Be forms tetrahedral complexes such as BeF_4^{2-} and $[Be(C_2O_4)]^{2-}$ and Al forms octahedral complexes like AlF_6^{3-} and $[Al(C_2O_4)_3]^{3-}$.

(*xiii*) Halides of both beryllium and aluminium have similar solubilities.

11. Which member of the alkaline earth metals family has
(*i*) least reactivity (*ii*) lowest density
(*iii*) highest boiling point (*iv*) maximum reduction potential?

12. Compare the first and second ionisation enthalpies of sodium and magnesium.

13. Arrange the following in the order of property mentioned :
(*i*) $BaCl_2$, $MgCl_2$, $BeCl_2$, $CaCl_2$
increasing ionic character
(*ii*) $Mg(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, $Ca(OH)_2$
increasing solubility in water
(*iii*) BeO, MgO, BaO, CaO
increasing basic character
(*iv*) $Mg(OH)_2$, $Ba(OH)_2$, $Ca(OH)_2$
increasing basic character

14. Answer the following :
(*i*) What is hydrolith ?
(*ii*) Which elements of alkaline earth metals family do not give characteristic flame colouration ?
(*iii*) Which out of NaOH or $Mg(OH)_2$ is stronger base ?
(*iv*) Which element in the group 2 is radioactive ?
(*v*) Which out of Mg^{2+}, Ba^{2+}, Ca^{2+} has maximum ionic mobility in water ?

Answers to Practice Problems

11. (*i*) Be (*ii*) Ca (*iii*) Be (*iv*) Be.

12. IE_1 : Na < Mg ; IE_2 : Na > Mg

13. (*i*) $BeCl_2$, $MgCl_2$, $CaCl_2$, $BaCl_2$
(*ii*) $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
(*iii*) BeO, MgO, CaO, BaO
(*iv*) $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$

14. (*i*) CaH_2 (*ii*) Be, Mg (*iii*) NaOH (*iv*) Radium
(*v*) Ba^{2+}.

USES OF ALKALINE EARTH METALS

The important uses of alkaline earth metals are summarized below :

Uses of beryllium

The important uses of beryllium are :

(*i*) Beryllium is used in the manufacture of many alloys. For example, copper–beryllium alloys are used in the preparation of high strength springs.

(*ii*) Metallic beryllium is used for making windows of X–ray tubes.

Uses of magnesium

The important uses of magnesium are :

(*i*) Magnesium is the lightest constructional metal in industry having a density less than two thirds of aluminium.

(*ii*) Magnesium is an important alloying metal. Some of the alloys of magnesium contain more than 90% Mg and 2–9% Al and 1% Zn. These alloys are used in automobile engines, making balances and in aircraft constructions. Upto 5% magnesium is added to most commercial aluminium alloys (*e.g.* duralumin, magnalium) to improve its resistance to corrosion, mechanical properties and weldability.

(*iii*) Magnesium is used for cathodic protection of other metals as oxygen scavenger.

(*iv*) It is used as a reducing agent in metallurgy for the production of certain metals such as Ti, Zr and Hf.

(*v*) Magnesium powder is used in flash powders and bulbs, incendiary bombs and signals.

(*vi*) Magnesium is used for the ignition of thermite charge in aluminothermy.

(*vii*) In the form of Grignard reagent, which is alkyl magnesium halide (RMgX), magnesium is useful in preparing a number of organic compounds.

(*viii*) The compounds of magnesium such as magnesium hydroxide and magnesium carbonate are used in making tooth pastes.

(*ix*) Magnesium hydroxide (milk of magnesia) is used as an antacid to neutralise excess of acid in stomach.

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(*x*) Magnesium is used as a deoxidizer for removing last traces of oxygen from copper, steel, etc.

Uses of calcium

The important uses of calcium are :

(*i*) Calcium is a powerful reducing agent and therefore, it is used for the extraction of metals from their oxides in metallurgy.

(*ii*) It is used to remove traces of air from vacuum tubes since it has strong affinity for both nitrogen and oxygen.

(*iii*) It is used to remove last traces of moisture from alcohol.

(*iv*) Compounds of calcium such as limestone and gypsum are used as constituents of cement and mortar.

(*v*) When alloyed with lead, it is used for cable coverings. When alloyed with aluminium, it is used in casting and forging.

Radium salts are used in radiotherapy such as for treatment of cancer.

SOME IMPORTANT COMPOUNDS OF CALCIUM

Alkaline earth metals form many compounds. The compounds of calcium are industrially important compounds. Some of these are discussed below :

1. Calcium oxide or Quicklime, CaO

Preparation

It is prepared on a commercial scale by heating limestone ($CaCO_3$) in a special type of rotary kiln at 1070 – 1270K.

$$CaCO_3 \underset{}{\overset{\text{Heat}}{\rightleftharpoons}} CaO + CO_2, \quad \Delta H = 179.9 \text{ kJ}$$

The necessary conditions for the good yield of quick lime are :

(*i*) Since the reaction is reversible, therefore, the carbon dioxide formed must be removed as soon as it is formed so that the reaction remains in the forward direction. In other words, it will not make the backward reaction possible. It is only above 1100 K that the gas escapes freely and therefore, a temperature of 1273 K is maintained.

(*ii*) The temperature should not be allowed to rise above 1273 K otherwise silica (SiO_2) present as impurity in limestone will react with calcium oxide to form calcium silicate.

$$CaO + SiO_2 \xrightarrow{\text{Above 1273 K}} \underset{\text{Calcium silicate}}{CaSiO_3}$$

Properties

(*i*) It is a white amorphous solid having melting point about 2870 K.

(*ii*) On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$CaO + CO_2 \longrightarrow CaCO_3$$

The reaction with water is highly exothermic :

$$CaO\,(s) + H_2O\,(l) \longrightarrow Ca(OH)_2\,(aq)$$
$$\Delta H = -64.5 \text{ kJ mol}^{-1}$$

(*iii*) It is usually obtained in the form of hard lumps. When heated in oxyhydrogen flame, it emits a brilliant white light known as *lime light*.

(*iv*) The addition of limited amount of water breaks the lump of lime. This process is called ***slaking*** of the lime and the product is called ***slaked lime***. Quicklime slaked with soda gives solid, **sodalime**.

(*v*) It combines with acidic oxides at high temperatures :

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

Uses of calcium oxide

(*i*) It is an important primary material and is the cheapest form of alkali.

(*ii*) It is used in the manufacture of sodium carbonate from caustic soda.

(*iii*) It is used as a flux in metallurgy.

(*iv*) It is used in the purification of sugar and in the manufacture of dye stuffs.

(*v*) It is used in drying gases and alcohol.

(*vi*) Calcium oxide is used as a building material.

2. Calcium hydroxide or Slaked lime, $Ca(OH)_2$

Preparation

(*i*) **From quicklime.** Calcium hydroxide is prepared by adding water to quicklime, CaO. This process is called *slaking of lime.*

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

(*ii*) **From calcium chloride.** It can also be obtained by treating caustic soda with calcium chloride.

$$CaCl_2 + 2NaOH \longrightarrow Ca(OH)_2 + 2NaCl$$

Properties

(*i*) It is a white amorphous powder and is sparingly soluble in water. The aqueous solution of calcium hydroxide is called *lime water*. The suspension of slaked lime in water is called **milk of lime.**

(*ii*) It is strongly basic and therefore, reacts with acids and acidic gases forming salts.

(*iii*) It reacts with chlorine to form bleaching powder.

$$Ca(OH)_2 + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{CaOCl_2} + H_2O$$

(*iv*) When carbon dioxide is passed through lime water, it becomes milky due to formation of calcium carbonate.

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{Milky}}{CaCO_3} + H_2O$$

The milkiness disappears on passing the gas in excess because calcium carbonate changes to a soluble bicarbonate.

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{\substack{\text{(Soluble)}\\ \text{Milkiness disappears}}}{Ca(HCO_3)_2}$$

(*v*) It dissolves in dilute hydrochloric acid.

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$$

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(*vi*) Milk of lime reacts with chlorine to form hypochlorite, which is a constituent of bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(ClO)_2 + 2H_2O$$

However, it is not soluble in dilute sulphuric acid because calcium sulphate formed is water insoluble salt.

Uses of calcium hydroxide

(*i*) Calcium hydroxide is used in the preparation of mortar, a building material.

(*ii*) It is used as a whitewash due to its disinfectant nature.

(*iii*) It is used for the softening of hard water.

(*iv*) It is used for the detection of carbon dioxide as lime water.

(*v*) It is used for absorbing acidic gases.

(*vi*) It is used for preparing ammonia from ammonium chloride.

(*vii*) It is used in glass making, tanning industry, for preparation of bleaching powder and for purification of sugar.

3. Calcium carbonate or Limestone or Marble, $CaCO_3$.

Calcium carbonate occurs in nature alongwith magnesium carbonate.

Preparation

(*i*) **From slaked lime.** It can be prepared by passing carbon dioxide through slaked lime in limited amount.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

It may be noted that excess of carbon dioxide should be avoided because this leads to the formation of water soluble calcium hydrogen carbonate.

(*ii*) **From calcium chloride.** It can be prepared by adding aqueous solution of sodium carbonate to **calcium chloride.**

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2NaCl$$

Properties

(*i*) It is a white fluffy solid and is almost insoluble in water.

(*ii*) When heated to 1200 K, it decomposes to evolve carbon dioxide.

$$CaCO_3 \xrightarrow{1200\ K} CaO + CO_2$$

(*iii*) It reacts with dilute acids to liberate carbon dioxide.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$
$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

Uses of calcium carbonate

(*i*) Calcium carbonate is used as a building material in the form of marble.

(*ii*) It is used in the manufacture of quicklime.

(*iii*) It is also used as a raw material for the manufacture of sodium carbonate in Solvay process.

(*iv*) It is used as a flux in the extraction of metals such as iron.

(*v*) Specially precipitated calcium carbonate is extensively used in the manufacture of high quality paper.

(*vi*) It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum and a filler in cosmetics.

4. Plaster of Paris,

$$(CaSO_4)_2 \cdot H_2O \text{ or } CaSO_4 \cdot \frac{1}{2}H_2O$$

Preparation

It is prepared by heating gypsum to 393 K.

$$2(CaSO_4.2H_2O) \xrightarrow{393\ K} (CaSO_4)_2.H_2O + 3H_2O$$

Thus, it contains one molecule of water for every two calcium and two sulphate ions. It may be noted that the temperature should not be allowed to rise because at 437K the whole of water is lost and the anhydrous salt left is called *dead burnt plaster.* It has no setting properties.

Properties

(*i*) It is a white powder.

(*ii*) On mixing with water, it forms a plastic mass which sets into a hard solid in 5-15 minutes. This is called **setting of plaster of paris**. The setting is due to hydration of plaster of paris into gypsum.

$$(CaSO_4)_2.H_2O + 3H_2O \longrightarrow \underset{\text{Gypsum}}{2CaSO_4.2H_2O}$$

During setting, there is a slight increase in volume. This helps plaster of paris to take the shape of any mould in which it is added.

Uses of plaster of paris

(*i*) Plaster of paris is used for producing moulds for pottery, ceramics, etc.

(*ii*) It is used for making statues, models and other decorative materials.

(*iii*) It is used in the building industry as well as plasters.

(*iv*) It is used in surgical bandages known as plasters for setting broken and fractured bones in the body because it immoblises the affected part of the organ where there is a bone fracture or sprain.

(*v*) It is also used in dentistry.

SOLVED EXAMPLES

❑ **Example 11.**

The enthalpy of formation of hypothetical CaCl (s) theoretically found to be –188 kJ mol^{-1} and $\Delta_f H°$ for $CaCl_2$ (s) is –795 kJ mol^{-1}. Calculate $\Delta_r H°$ for the disproportion reaction :

$2CaCl\ (s) \longrightarrow CaCl_2\ (s) + Ca\ (s)$

Solution: The given equations are :

(*i*) $Ca\ (s) + Cl_2\ (g) \longrightarrow CaCl_2\ (s)$
$\Delta_f H° = -795$ kJ mol^{-1}

(*ii*) $Ca\ (s) + \frac{1}{2}Cl_2\ (g) \longrightarrow CaCl\ (s)$
$\Delta_f H° = -188$ kJ mol^{-1}

(*iii*) or $2Ca\ (s) + Cl_2\ (g) \longrightarrow 2CaCl\ (s)$
$\Delta H° = -376$ kJ mol^{-1}

Subtracting (*iii*) from (*i*)

$\Delta_r H°$ for disproportion reaction is

$2CaCl\ (s) \longrightarrow CaCl_2\ (s) + Ca\ (s)$

$\Delta_r H° = -795 - (-376)$

$= -419$ kJ

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❑ **Example 12.**

What happens when

(i) Magnesium is burnt in air
(ii) Quicklime is heated with silica
(iii) Calcium nitrate is heated
(iv) Chlorine reacts with slaked lime

N.C.E.R.T.

Solution: (*i*) When magnesium is burnt in air, it gives brilliant flame forming magnesium oxide and magnesium nitride.

$$2Mg + O_2 \longrightarrow 2MgO$$
$$3Mg + N_2 \longrightarrow Mg_3N_2$$

(*ii*) When quicklime is heated with silica, it gives calcium silicate.

$$CaO + SiO_2 \xrightarrow{\text{above 1273 K}} \underset{\text{Cal. silicate}}{CaSiO_3}$$

(*iii*) When calcium nitrate is heated, it gives CaO, NO_2 and O_2.

$$2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$$

(*iv*) Chlorine reacts with slaked lime to form calcium hypochlorite, $Ca(OCl)_2$ which is a constituent of bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{CaCl_2 + Ca(OCl)_2}_{\text{Bleaching powder}} + 2H_2O$$

❑ **Example 13.**

Arrange the following in the decreasing order of the property mentioned :

(i) Li^+, Na^+, K^+, Rb^+ (Ionic mobility)
(ii) Be, Mg, Ca, Sr (Melting point)
(iii) BeO, MgO, CaO (Enthalpy of formation)
(iv) Be, Mg, Ca (Metallic radius)

Solution:

(*i*) $Rb^+ > K^+ > Na^+ > Li^+$ (*ii*) Be > Ca > Sr > Mg
(*iii*) CaO > MgO > BeO (*iv*) Ca > Mg > Be

❑ **Example 14.**

Name one reagent or one operation to distinguish between :

(i) $BeSO_4$ and $BaSO_4$ (ii) $Be(OH)_2$ and $Ba(OH)_2$

Solution: (*i*) $BeSO_4$ is soluble in water while $BaSO_4$ is insoluble.

(*ii*) $Be(OH)_2$ dissolves in NaOH while $Ba(OH)_2$ is insoluble.

❑ **Example 15.**

Complete the following equations for the reaction between :

(i) $Ca + H_2O$ (ii) $Ca(OH)_2 + Cl_2$
(iii) $BeO + NaOH$ (iv) $BaO_2 + H_2SO_4$

Solution:

(*i*) $Ca + 2H_2O \xrightarrow{\text{Heat}} Ca(OH)_2 + H_2$

(*ii*) $Ca(OH)_2 + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{CaOCl_2} + H_2O$

(*iii*) $BeO + 2NaOH \longrightarrow \underset{\text{Sodium Beryllate}}{Na_2BeO_2} + H_2O$

(*iv*) $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$.

❑ **Example 16.**

Why does the solubility of alkaline earth metal carbonates and sulphates decrease down the group?

N.C.E.R.T.

Solution: In carbonates and sulphates, the size of the anion is much larger as compared to cations and the lattice enthalpy remains almost constant within a particular group. Since with the increase in size of the cation down the group, the hydration enthalpies decrease, the solubility will also decrease. Therefore, solubility of alkaline earth metal carbonates and sulphates decreases down the group.

❑ **Example 17.**

Why does solubility of alkaline earth metal hydroxides increase down the group?

N.C.E.R.T.

Solution: If the cation and anion are of comparable size, the anion being common, the radius of cation will influence the lattice enthalpy. In the group, both the lattice enthalpy and hydration enthalpy decrease with increase in size of the cation. But the decrease in lattice enthalpy is much more than the hydration enthalpy with increasing ionic size and hence, solubilty will increase as we go down the group. Therefore, the solubility of alkaline earth metal hydroxides increases down the group.

❑ **Example 18.**

When water is added to compound (A) of calcium, solution of compound (B) is formed. When carbon dioxide is passed into the solution, it turns milky due to the formation of compound (C). If excess of carbon dioxide is passed into the solution milkiness disappears due to the formation of compound (D). Identify the compounds A, B, C and D. Explain why the milkiness disappears in the last step. *(NCERT Exemplar Problem)*

Solution: The compound A is calcium oxide, CaO and B is calcium hydroxide, $Ca(OH)_2$.

The compound C is calcium carbonate, $CaCO_3$ and the compound D is calcium bicarbonate, $Ca(HCO_3)_2$. Calcium bicarbonate $Ca(HCO_3)_2$ is soluble in water and therefore, milkiness of solution disappears on passing excess of carbon dioxide into the solution.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{(Milkiness)}}{CaCO_3} + H_2O$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{\substack{\text{soluble}\\ \text{(Milkiness disappears)}}}{Ca(HCO_3)_2}$$

Practice Problems

15. What is (*i*) dolomite (*ii*) milk of lime ?
16. Name any two ores of magnesium.
17. What is dead burnt plaster ?
18. What is the formulae of
(*i*) Plaster of Paris (*ii*) Gypsum ?
19. What is magnesia ?
20. Why does a tube containing lime water turns milky when exhaling is made into it ?
21. Name three forms of calcium carbonate.
22. What happens when gypsum is heated to 390 K ?
23. What happens when carbon dioxide is passed through lime water ?
24. Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes milky on bubbling carbon dioxide. Identify A, B, C and D.

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Answers to Practice Problems

15. (*i*) $CaCO_3 . MgCO_3$ (*ii*) Suspension of calcium hydroxide in water.

16. Magnesite ($MgCO_3$), Dolomite ($MgCO_3 . CaCO_3$)

17. It is anhydrous calcium sulphate ($CaSO_4$).

18. (*i*) $(CaSO_4)_2 . H_2O$ (*ii*) $CaSO_4 . 2H_2O$

19. Magnesium oxide (MgO)

20. Due to the formation of calcium carbonate.

21. Limestone, chalk, marble.

22. Plaster of paris is formed as

$$2CaSO_4.2H_2O \xrightarrow{390\ K} (CaSO_4)_2 . H_2O + 3H_2O$$

23. Milkiness appears (due to $CaCO_3$) which disappears on passing excess of CO_2 [(due to the formation of $Ca(HCO_3)_2$]

24.

$$\underset{(A)}{3Ca} + N_2 \longrightarrow \underset{(B)}{Ca_3N_2} \xrightarrow{6H_2O} \underset{(C)}{3Ca(OH)_2} + \underset{(D)}{2NH_3}$$

$$\underset{(C)}{Ca(OH)_2} \xrightarrow{CO_2} \underset{\text{Milky}}{CaCO_3} + H_2O$$

INDUSTRIAL USES OF LIMESTONE AND LIME

Limestone rock is the common form of calcium carbonate, which also occurs as chalk, marble, calcite, argonite, etc. It also occurs as dolomite with magnesium. Limestone and dolomite are widely used as building materials on a large scale throughout the world. $CaCO_3$ is a major industrial chemical and is important for the production of quicklime (CaO) and slaked lime [$Ca(OH)_2$]. These chemicals have wide applications in chemical, metallurgical and construction industry. Some of the important industrial uses of lime and limestone are given below:

(*i*) Lime is an important constituent of Portland cement which is obtained by roasting limestone and sand with clay.

(*ii*) Large quantities of lime are used in the steel industry, where it is used as a flux to remove P, S, Si, Mn, etc. Lime is also used as a lubricant in steel wire drawing and in neutralising wastes.

(*iii*) It has also been used in the production of magnesium in Dow's process.

(*iv*) Lime is used in the chemical treatment of potable and industrial water supplies. It is also used with iron or alum to coagulate suspended solids and remove turbidity. It is also commonly used in water softening to remove temporary hardness. The common reactions occurring during water softening are :

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3\downarrow + CaCO_3\downarrow + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow, \text{ etc.}$$

(*v*) Lime is used in scrubbers to remove SO_2 and H_2S from stack gases of fossil fuels in power generating stations and metallurgical smelters.

(*vi*) Lime is used in chemical industries such as manufacture of calcium carbide (for obtaining acetylene), cyanamide and other chemicals.

(*vii*) Lime is also used in the manufacture of glass.

(*viii*) Lime is used for manufacture of insecticides, calcium arsenate and fungicides such as Bordeaux mixtures [$CuSO_4/Ca(OH)_2$].

(*ix*) Paper and pulp industries consume large quantities of $Ca(OH)_2$ and $CaCO_3$. Bleaching liquor, calcium hypochlorite is obtained by reacting lime and chlorine. It is used for bleaching paper pulp.

Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper. This is obtained by calcining limestone and collecting the carbon dioxide and calcium oxide separately. The latter is then hydrated and re-carbonated to get the desired product

$$CaCO_3 \xrightarrow{Heat} CaO + CO_2$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

(*x*) $CaCO_3$ has domestic and pharmaceutical applications. Some of these are : as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, source of calcium enrichment in diets, a filler in cosmetics.

(*xi*) Lime also finds applications in dairy industry.

CEMENT*

Cement is one of the most important building materials. It was first introduced in England in 1824 by *Joseph Aspdin.* It is also called **Portland cement** because it resembles with the famous building stone found near Portland in England. In India, the cement industry started in 1914. Now India is producing above 100 million tonnes of cement annually (1999–2000). Chemically, it is *a finely ground mixture of calcium silicates and aluminates which set to a hard mass when treated with water.*

Composition of Cement

The average composition of cement is

CaO = 50 — 60%	MgO = 2—3%
SiO_2 = 20—25%	Fe_2O_3 = 1—2%
Al_2O_3 = 5—10%	SO_3 = 1—2%

* *Not in the syllabus of CBSE*

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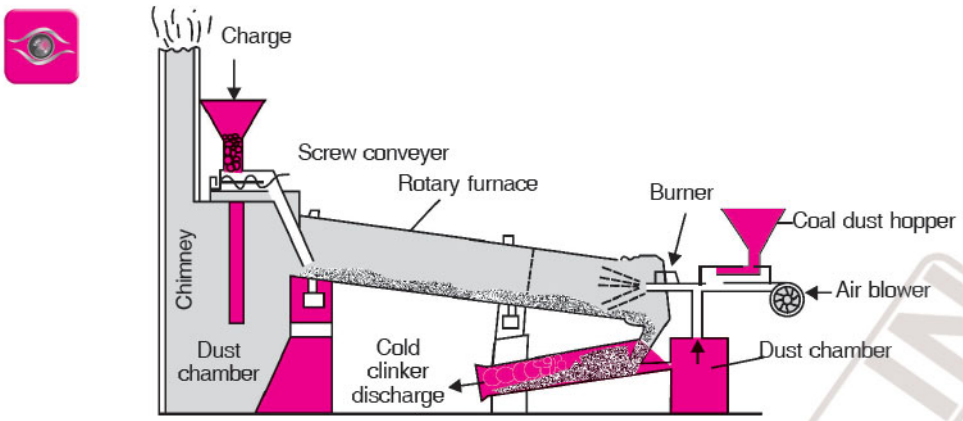

Fig. 7. Manufacture of cement.

For a good quality cement the ratio of silica (SiO_2) and alumina (Al_2O_3) should be between 2.5 to 4.0. Similarly, the ratio of lime (CaO) to the total oxide mixtures consisting of SiO_2, Al_2O_3 and Fe_2O_3 should be roughly 2 : 1. If lime is in excess, the cement cracks during setting. On the other hand, if lime is less than the required, the cement is weak in strength. Therefore, a proper composition of cement must be maintained to get cement of good quality.

Manufacture of Cement

The main raw materials for the manufacture are *limestone* and *clay*. The former supplies lime while the latter is the source of silica, alumina and iron oxide. The process involves the following steps :

(*i*) The powdered limestone (3 parts) and clay (1 part) are mixed.

(*ii*) The mixture is heated at about 1770–1870 K in a rotary kiln (Fig. 7). In this kiln, the temperature varies between 1100–1800 K. In this process, the following changes occur :

(*i*) *Limestone decomposes to give lime and* CO_2.

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

(*ii*) *Lime (obtained from limestone), alumina and silica (constituents of clay) react together to form a mixture of calcium silicate* ($2CaO.SiO_2$, $3CaO.SiO_2$) *and calcium aluminate* ($3CaO\,Al_2O_3$, $4CaO.Al_2O_3$).

The reactions taking place are :

$$2CaO + SiO_2 \longrightarrow \underset{\text{Dicalcium silicate}}{2CaO\,.\,SiO_2}$$

$$3CaO + SiO_2 \longrightarrow \underset{\text{Tricalcium silicate}}{3CaO\,.\,SiO_2}$$

$$3CaO + Al_2O_3 \longrightarrow \underset{\text{Tricalcium aluminate}}{3CaO\,.\,Al_2O_3}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\text{Tetracalcium aluminoferrite}}{4CaO\,.\,Al_2O_3\,.\,Fe_2O_3}$$

Due to very high temperature in this zone, about 20–30% mass melts and combines with solid mass to form pebbles known as **cement clinkers**.

The hot clinkers are cooled and are mixed with 2 to 3 per cent by weight of gypsum ($CaSO_4.2H_2O$). It is finely powdered and the powder is called Portland cement. The gypsum slows down the setting of cement so that its gets sufficiently hardened.

The important compounds present in Portland cement are :

Dicalcium silicate : (Ca_2SiO_4) : 26%

Tricalcium silicate (Ca_3SiO_5) : 51%

Tricalcium aluminate ($Ca_3Al_2O_6$) : 11%

Setting of cement. When cement is to be used, it is always mixed with water. It is an exothermic reaction and the cement reacts with water to form a gelatinous mass which slowly sets into a hard mass having —Si—O—Si— and—Si—O—Al— chains.

Uses. Cement is used as an important constructional material. It is used in concrete and reinforced concrete, in plastering and in construction of buildings, bridges and dams.

Next to iron and steel, it has become as a commodity of national necessity for any country.

In the present industrial age, demand of cement is increasing day by day. Huge structures of building cannot be erected without cement. Attempts have been made to find a substitute of cement. One of these is *fly ash* which is a waste product from the steel industry. This can be added to the cement to reduce its cost but at the same time it does not degrade its quality. In many countries, cement is made from rice husk with high silica contents.

BIOLOGICAL IMPORTANCE OF CALCIUM AND MAGNESIUM

On an average an adult body contains about 25 g of Mg and 1200 g of Ca as compared to only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200–300 mg.

Magnesium and calcium play important role in biological processes. Mg^{2+} ions are concentrated in animal cells and Ca^{2+} are concentrated in body fluids outside the cells in much a similar way that K^+ concentrates inside the cells and Na^+ outside.

All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. Mg^{2+} ions form a

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complex with ATP and are constituents of phosphohydrolases and phosphotransferases, which are enzymes for reactions involving ATP and energy release. They are very essential for the transmission of impulses along nerve fibres. Mg^{2+} ions are also present in chlorophyll which is the green colouring pigment present in plants. Chlorophyll absorbs light from the sun and carries the process of *photosynthesis* in plants.

Ca^{2+} ions play a significant role in skeletal formation. With phosphorus in the mineral hydroxyapatite, $Ca_5(PO_4)_3OH$ it is the major constituent of bones, teeth and shells. About 99% of body calcium is present in bones and teeth. The calcium concentration in plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones *calcitonin* and *parathyroid* hormone. It is important to know that bone is not an inert and unchanging substance but it is continuously being solubilized and redeposited to the extent of 400 mg per day in man. All this calcium passes through the plasma. In addition to skeletal role, Ca^{2+} ions play many biochemical roles in neuromuscular function, interneuronal transmission, cell membrane integrity blood coagulation, etc. Some of these are :

(*i*) It acts as a messenger for hormonal action.
(*ii*) It acts as a trigger for muscular contraction.
(*iii*) It acts as initiator for blood clotting.
(*iv*) It plays a role in the stabilization of protein structure.
(*v*) It helps in the maintenance of rhythm of heart.

add on Conceptual Questions 2

CONCEPTUAL QA

Q.1. Mg^{2+} is much more heavily hydrated than Na^+. Why ?
Ans. The extent of hydration depends upon the charge density. Mg^{2+} ion is smaller in size than Na^+ and has twice the charge than that of Na^+. Hence, Mg^{2+} has higher charge density than Na^+ and therefore, is heavily hydrated.

Q.2. Why are halides of beryllium polymeric ?
Ans. The halides of Be are electron deficient as their octets are incomplete. Therefore, to complete their octets, the halides polymerize.

Q.3. What is difference between quicklime, slaked lime and lime water ?
Ans. Quicklime is CaO, slaked lime is $Ca(OH)_2$ and lime water is an aqueous solution of $Ca(OH)_2$.

Q.4. What is dead burnt plaster ? How is it obtained ?
Ans. Dead burnt plaster is anhydrous $CaSO_4$. It is obtained by heating plaster of Paris.

$$\underset{\text{Plaster of Paris}}{CaSO_4 \cdot \frac{1}{2}H_2O} \xrightarrow{450\ K} \underset{\text{Dead burnt plaster}}{CaSO_4 + \frac{1}{2}H_2O}$$

Q.5. Magnesium metal burns in air to form a white ash. On treating the white ash with water, odour of ammonia is detected. Explain.
Ans. Mg burns in air to form MgO and Mg_3N_2.

$$2\,Mg + O_2 \longrightarrow 2MgO$$
$$3\,Mg + N_2 \longrightarrow Mg_3N_2$$

Magnesium nitride on hydrolysis given ammonia.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

Q. 6. A piece of burning magnesium continues to burn in SO_2. Explain.
Ans. A piece of magnesium continues to burn in SO_2 because it reacts with it to form MgO and S.

$$2\,Mg + SO_2 \longrightarrow 2\,MgO + S$$

This reaction is exothermic and it keeps the piece of magnesium burning.

Q.7. $BeCl_2$ can be easily hydrolysed. Explain.
Ans. $BeCl_2$ can be easily hydrolysed because it is electron deficient compound.

$$BeCl_2 + 4H_2O \longrightarrow [Be(H_2O)_4]Cl_2$$

Q.8. Arrange the alkaline earth metal carbonates in the decreasing order of thermal stability.
Ans. The decreasing order of thermal stability is

$$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$$

Q.9. Which of the following has highest solubility in each of the following :
(*i*) $BaSO_4$, $MgSO_4$, $CaSO_4$ (*ii*) $Mg(OH)_2$, $Ba(OH)_2$, $Ca(OH)_2$
Ans. (*i*) $MgSO_4$ (*ii*) $Ba(OH)_2$

Q.10. Arrange the following sulphates of alkaline earth metals in order of decreasing thermal stability: $BeSO_4$, $MgSO_4$, $CaSO_4$, $SrSO_4$.
Ans. $SrSO_4 > CaSO_4 > MgSO_4 > BeSO_4$.

Q.11. Why does beryllium show similarities with aluminium ? *N.C.E.R.T.*

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Ans. Beryllium shows similarities with aluminium because of same electronegativity (1.5) and very similar polarizing power *i.e.*, charge/radius ratio (Be^{2+} = 2/31 = 0.064, Al^{3+} = 3/50 = 0.060) of their ions.

CONCEPTUAL QA

Q.12. The second ionization enthalpy of calcium is more than that of first and yet calcium forms $CaCl_2$ not CaCl. Why ? *N.C.E.R.T.*

Ans. The higher enthaply of lattice formation of Ca^{2+} is more than compensates the second ionisation enthalpy required for the formation of divalent Ca^{2+} ions.

Q.13. Explain why alkali and alkaline earth metals can not be obtained by chemical reduction methods?

Ans. Alkali and alkaline earth metals are themselves very strong reducing agents and, therefore, cannot be reduced.

Q.14. Beryllium and magnesium donot give colour to flame whereas other alkaline earth metals do so why?

Ans. Beryllium and magnesium atoms in comparison to other alkaline earth metals are comparatively smaller and their ionisation enthalpies are very high. Hence, the energy of the flame is not sufficient to excite their electrons to higher energy levels. These elements, therefore, do not give any colour in Bunsen flame.

Q.15. Mg^{2+} is much hydrated than Na^+. Why?

Ans. The extent of hydration depends upon the charge density *i.e.*, charge/size. Mg^{2+} ion is smaller in size than Na^+ ion and has twice the charge than Na^+. Therefore, its charge density is high and hence is extensively hydrated.

Q.16. An element of group 2 forms covalent oxide which is amphoteric in nature and dissolves in water to give an amphoteric hydroxide. Name the element.

Ans. Beryllium.

Q.17. Name an element of group 2 which forms an amphoteric oxide and water soluble sulphate. To which period, does it belong?

Ans. Beryllium. It belongs to second period.

Q.18. What is epsom salt? What is the action of heat on it?

Ans. Epsom salt is $MgSO_4.\ 7H_2O$.

Action of heat: $MgSO_4.\ 7H_2O \xrightarrow[-6H_2O]{423\ K} MgSO_4.\ H_2O \xrightarrow[-H_2O]{573\ K} MgSO_4 \xrightarrow{Heat} MgO + SO_3$

Q.19. How will you distinguish between $BaSO_4$ and $BeSO_4$?

Ans. $BeSO_4$ is soluble in water but $BaSO_4$ is insoluble in water.

Q.20. Which of the two: $MgCO_3$ or $CaCO_3$ is more stable?

Ans. $CaCO_3$.

Chapter Summary

Key Terms

- **s-block elements.** The elements in which the last electron enters the outermost *s*-orbital.
- **Diagonal relationship.** The similarity in properties of elements present diagonally in different groups.
- **Polarisation.** The distortion of the electron cloud of the negative ion by positive ion.

QUICK CHAPTER ROUND UP

s-Block Elements
[Noble gas]$ns^{1\text{ or }2}$

Group I : Alkali metals : [Noble gas]ns^1
Li, Na, K, Rb, Cs, Fr

- show +1 oxidation state
- give characteristic flame colourations due to their low ionisation enthalpies
- exhibit photoelectric effect (except Li)
- Basic character:
  LiOH < NaOH < KOH < RbOH < CsOH

Group II : Alkaline earth metals : [Noble gas]ns^2

- Be, Mg, Ca, Sr, Ba, Ra
- show +2 oxidation state
- except Be and Mg, they give characteristic flame colourations.
- Basic character:
  $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

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- get tarnished in moist air and are kept under kerosene oil, benzene, hexane
- On burning lithium forms monoxide (Li_2O), sodium forms the peroxides (Na_2O_2), the other elements form superoxides (MO_2: M = K, Rb, Cs).

$4Li + O_2 \longrightarrow Li_2O$ (monoxide)
$2Na + O_2 \longrightarrow Na_2O_2$ (peroxide)
$M + O_2 \longrightarrow MO_2$ (superoxide)
(M = K, Rb, Cs)

This is because small cation can stabilize small anion and large cation can stabilize large anion.

- Ionic radii of alkali metals :
  $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$
- Enthalpy of hydration :
  $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
- Ionic radii of hydrated alkali metal ions :
  $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Ionic radii of hydrated Li^+ is largest because the value of charge/size for Li^+ is highest. Hence, it is hydrated to the greatest extent.

- Ionic mobility in water :
  $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$
- Solutions of alkali metals in liquid NH_3 are highly conducting and deep blue in colour.
- The blue colour is due to the presence of ammoniated electrons.
- Alkali metals are strong reducing agents and reducing character increases down the group (except Li, which is strongest reducing agent due to its high oxidation potential).
- Fluorides of alkali metals are most stable while iodides are least stable.

Compounds of alkali metals

- Sodium carbonate (washing soda)
  $Na_2CO_3.10H_2O$
  Preparation : Solvay process

$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$
$(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2NH_4HCO_3$
$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$
$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3 + CO_2 + H_2O$

- Sodium chloride (NaCl)
  Obtained by solar evaporation of sea water.
- Sodium hydroxide or caustic soda (NaOH)
  commercially obtained by electrolysis of an aqueous solution of sodium chloride using mercury cathode and graphite anode, (Castner Kellner Cell)
- Sodium bicarbonate (baking soda) $NaHCO_3$.
  prepared by saturating sodium carbonate solution with CO_2.

$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$

- Alkaline earth metals react with air or O_2 slowly upon heating to form oxides MO.
- Powdered Be burns brilliantly to give BeO and Be_3N_2.

$2Be + O_2\,(air) \longrightarrow 2BeO$
$3Be + N_2\,(air) \longrightarrow Be_3N_2$

- Alkaline earth metals react with acids and evolve H_2.
- Be is amphoteric and reacts with HCl and NaOH.
- Solubility decreases :
  $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > CaSO_4$;
  $BaCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
- Oxides are

BeO	MgO	CaO, SrO, BaO
Amphoteric	Weakly basic	Basic

- $BeCl_2$ is covalent while $MgCl_2$ and $CaCl_2$ are ionic.
- Beryllium halides are covalent while all other halides are ionic and are readily soluble in water.
- $BeCl_2$ in vapour phase exist as dimer which dissociates to linear monomer at 1200 K.
- In solid state, $BeCl_2$ has polymeric chain structure

Compounds of alkaline earth metals

- **Calcium oxide or Quick lime (CaO)**
  obtained by heating limestone

$CaCO_3 \underset{}{\overset{\text{Heat}}{\rightleftharpoons}} CaO + CO_2$

- **Calcium hydroxide or slaked lime [$Ca(OH)_2$]**
  On adding water to CaO, calcium hydroxide is formed.
  $CaO + H_2O \longrightarrow Ca(OH)_2$
  It is called **slaking of lime.**
- When CO_2 is passed through **lime water**, milkiness is formed (due to $CaCO_3$) and on further passing CO_2 gas, milkiness disappears [due to $Ca(HCO_3)_2$].
- **Calcium carbonate or limestone ($CaCO_3$)**

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$
$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2NaCl$

- **Plaster of paris** $CaSO_4.\frac{1}{2}H_2O$

$2(\underset{\text{Gypsum}}{CaSO_4.2H_2O}) \longrightarrow (CaSO_4)_2\,H_2O + 3H_2O$

- On mixing with water, it forms a plastic mass which sets into a hard solid mass (gypsum). This is called setting of Plaster of Paris.
- $2CaSO_4.\frac{1}{2}H_2O + 3H_2O \longrightarrow \underset{\text{Gypsum}}{2CaSO_4.2H_2O}$

Diagonal relationship

Li—Mg and Be—Al

- $BeCl_2$ and $AlCl_3$ behave as strong Lewis acids and are soluble in organic solvents.
- Both Be and Al form fluoro complex ions *i.e.* BeF_4^{2-} and AlF_4^- in solution.

- Na^+, K^+, Mg^{2+} and Ca^{2+} are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

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NCERT FILE Solved

NCERT Textbook Exercises

Q.1. What are the common physical and chemical features of alkali metals?

Ans. *Refer text page 3–4.*

Q. 2. Discuss the general characteristics and gradation in properties of alkaline earth metals.

Ans. *Refer text page 21.*

Q.3. Why are alkali metals not found in nature?

Ans. Alkali metals are highly reactive and therefore, are not found in nature. They are present in the combined state in the form of halides, oxides, silicates, borates, nitrates, etc.

Q. 4. Find out the oxidation state of sodium in Na_2O_2.

Ans. Let x is the oxidation state of sodium. Since Na_2O_2 contains a peroxide linkage in which oxygen has oxidation state of –1,

$$\underset{Na_2}{x} \qquad \underset{O_2}{-1}$$

$$2x + 2(-1) = 0 \quad \text{or } x = +1$$

Q. 5. Explain why is sodium less reactive than potassium.

Ans. The ionisation enthalpy of potassium (496 kJ mol^{-1}) is less than that of sodium (520 $kJmol^{-1}$) and therefore, potassium is more reactive than sodium. This is also indicated by more negative standard electrode potential of potassium (–2.925 V) as compared to sodium (–2.714V).

Q. 6. Compare the alkali metals and alkaline earth metals with respect to (*i*) ionisation enthalpy (*ii*) basicity of oxides and (*iii*) solubility of hydroxides.

Ans. (*i*) **Ionisation enthalpy.** Ionisation enthalpies of alkaline earth metals are higher than those of alkali metals. This is because of smaller size of alkaline earth metal corresponding to alkali metal of the same period.

(*ii*) The oxides of alkali and alkaline earth metals dissolve in water to form their respective hydroxides. These oxides are strong bases. However, the oxides of alkali metals are more basic than those of alkaline earth metals. This is because the ionization enthalpy of alkali metals is lower or the electropositive character of alkali metals is higher than that of corresponding alkaline earth metal so that M—OH bond in alkali metals can more easily ionize.

$$MOH \longrightarrow M^+ + OH^-$$

(*iii*) Because of small size and high charge, the lattice enthalpies of alkaline earth metals are much more than those of alkali metals and therfore, the solubility of alkaline earth metal hydroxides is less than that of alkali metals.

Q. 7. In what ways lithium shows similarities to magnesium in its chemical behaviour?

Ans. *Refer text page 10.*

Q. 8. Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods?

Ans. Alkali and alkaline earth metals are themselves very strong reducing agents (high reduction potential values). Therefore, they cannot be isolated by reduction of their oxides or other compounds.

Q.9. Why are potassium and cesium, rather than lithium used in photoelectric cells?

Ans. Potassium and cesium have much lower ionization enthalpy than that of lithium. Therefore, these metals on exposure to light, easily emit electrons but lithium does not. Therefore, K and Cs rather than Li are used in photoelectric cells.

Q. 10. When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reasons for this type of colour change.

Ans. The dilute solutions of alkali metals in liquid ammonia are blue. As the concentration increases, the colour changes to bronze. The blue colour of alkali metals is due to the ammoniated electrons.

$$\underset{\text{Alkali metal}}{M} + (x+y)\,NH_3 \longrightarrow \underset{\text{Ammoniated electron}}{[M(NH_3)_x]^+ + [e(NH_3)_y]^-}$$

However, when the concentration increases, the ammoniated metal ions may get bound by free electrons and the colour becomes copper bronze.

$$2e^-(NH_3)_y \longrightarrow [e^-(NH_3)_y]_2$$

Q. 11. Beryllium and magnesium donot give colour to flame whereas other alkaline earth metals do so. Why?

Ans. *Refer Conceptual Questions* 2 *Q.14. (Page 36)*

Q. 12. Discuss the various reactions that occur in the Solvay process.

Ans. In Solvay process, carbon dioxide is passed through a brine solution (about 28% NaCl) saturated with ammonia to give sodium bicarbonate.

$$2NH_3 + H_2O + CO_2 \longrightarrow \underset{\text{Amm. carbonate}}{(NH_4)_2CO_3}$$

$$(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Amm. bicarbonate}}{2NH_4HCO_3}$$

$$\underset{\text{Brine}}{NH_4HCO_3 + NaCl} \longrightarrow \underset{\text{Sod. bicarbonate (ppt.)}}{NaHCO_3} + NH_4Cl$$

The precipitated sodium bicarbonate is filtered and dried. It is ignited to give sodium carbonate.

$$2NaHCO_3 \xrightarrow{\text{Heat}} \underset{\text{Sodium carbonate}}{Na_2CO_3} + CO_2 + H_2O$$

The carbon dioxide required for the reaction is prepared by heating limestone ($CaCO_3$) to about 1300 K in a lime kiln. Lime formed is dissolved in water to get calcium hydroxide which is transferred to the ammonia recovery tower.

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$$CaCO_3 \xrightarrow{Heat} \underset{\text{Calcium oxide (lime)}}{CaO} + CO_2$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Ammonia needed for the purpose is prepared by heating ammonium chloride obtained above with calcium hydroxide.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

Therefore, the only by product of the reaction is $CaCl_2$.

Q.13. Potassium carbonate cannot be prepared by Solvay process. Why?

Ans. Potassium carbonate cannot be prepared by Solvay process because potassium bicarbonate being more soluble than sodium bicarbonate does not get precipitated when CO_2 is passed through a concentrated solution of KCl saturated with NH_3.

Q.14. Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

Ans. Lithium is less electropositive than sodium and therefore, carbonate of lithium is less stable than that of sodium. Li_2CO_3 is not so stable to heat and therefore, decomposes at lower temperature. This is because lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of Li_2O and CO_2. On the other hand, Na_2CO_3 is very stable and decomposes at higher temperature.

Q. 15. Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals. (*a*) Nitrates (*b*) Carbonates (*c*) Sulphates.

Ans. **Solubility.** (*a*) Nitrates, carbonates and sulphates of alkali metals are soluble in water. Their solubility in water increases on moving down the group because their lattice enthalpies decrease more rapidly than the hydration enthalpies.

(*b*) On the other hand, nitrates of alkaline earth metals are soluble in water. However, their solubility decreases down the group because their hydration enthalpies decrease more rapidly than the lattice enthalpies.

The carbonates and sulphates of alkaline earth metals are less soluble than corresponding alkali metals. Their solubility decreases down the group due to decrease in hydration enthalpy.

Thermal stability. (*a*) Nitrates of both alkali metals and alkaline earth metals decompose on heating. Alkaline earth metals nitrates on heating give metal oxide, NO_2 and oxygen. The nitrates of Na, K, Rb and Cs decompose to give metal nitrites and oxygen.

$$2M(NO_3)_2 \xrightarrow{\Delta} 2MO + 4NO_2 + O_2$$

(M = Be, Mg, Ca, Sr, Ba)

$$2MNO_3 \xrightarrow{\Delta} 2MNO_2 + O_2$$

(M = Na, K, Rb, Cs)

Lithium nitrate decomposes like $Mg(NO_3)_2$ to form metal oxide, NO_2 and O_2.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

This is because Li^+ being small in size cannot stabilize large NO_3^- ion.

(*b*) The carbonates of alkaline earth metals are relatively less stable towards heat and decompose to CO_2.

$$MCO_3 \longrightarrow MO + CO_2$$

(M = Be, Mg, Ca, Sr, Ba)

However, their stability increases as we move down the group. The temperature at which these carbonate decompose are:

$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
< 373 K	813K	1173K	1563K	1635K
	Thermal stability increases $\longrightarrow$			

Li_2CO_3 decomposes similar to $MgCO_3$ because of diagonal relationship.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

All other alkali metal carbonates are stable and donot decompose readily.

(*c*) Sulphates of alkaline earth metals decompose on heating and give SO_3.

$$MSO_4 \xrightarrow{\Delta} MO + SO_3$$

The stability of sulphates of alkaline earth metals increases as the electropositive character of the metals increases.

$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$
773K	1168K	1422K	1644K

Among alkali metal sulphates Li_2SO_4 decomposes like $MgSO_4$ to give SO_3.

$$Li_2SO_4 \xrightarrow{\Delta} Li_2O + SO_3$$

$$MgSO_4 \xrightarrow{\Delta} MgO + SO_3$$

Other alkali metal sulphates are stable to heat and donot decompose easily.

Q.16. Starting with sodium chloride how would you proceed to prepare (*i*) sodium metal (*ii*) sodium hydroxide (*iii*) sodium peroxide (*iv*) sodium carbonate?

Ans. (*i*) Sodium metal is manufactured by electrolysis of a fused mixture of NaCl (40%) and $CaCl_2$ (60%) in Down cell at 873K using graphite anode and iron cathode. Sodium is liberated at the anode while Cl_2 is evolved at cathode

At cathode : Na^+ (melt) + $e^- \longrightarrow Na\ (l)$

$$2Cl^-(melt) \longrightarrow Cl_2 + 2e^-$$

(*ii*) Sodium hydroxide is manufactured by electrolysis of sodium chloride (brine) in Castner Kellner cell, using carbon anode and mercury cathode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam while Cl_2 gas is evolved at the anode.

Cathode : $Na^+ + e^- \longrightarrow Na$

$$2Na + Hg \longrightarrow NaHg\ (amalgam)$$

Anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

The amalgam reacts with water to give NaOH and H_2 gas is evolved.

$$2NaHg + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$$

(*iii*) Sodium peroxide is manufactured by heating sodium in excess of oxygen. The initially formed sodium oxide reacts with more oxygen to form Na_2O_2.

$$2Na + \frac{1}{2}O_2 \longrightarrow Na_2O$$

$$2Na_2O + O_2 \longrightarrow 2\,Na_2O_2$$

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(*iv*) Sodium carbonate is obtained by Solvay process. For details *refer answer* to Q. 12.

Q.17. What happens when

(*i*) magnesium is burnt in air

(*ii*) quick lime is heated with silica

(*iii*) chlorine reacts with slaked lime

(*iv*) calcium nitrate is heated

Ans. *Refer Solved Example 12. (Page 32)*

Q. 18. Describe two important uses of each of the following: (*i*) caustic soda (*ii*) sodium carbonate (*iii*) quick lime.

Ans. (*a*) **Caustic soda**

(*i*) It is used in the manufacture of soap, paper, artificial silk and other chemicals.

(*ii*) It is used in the textile industry for mercerising cotton fabrics.

(*b*) **Sodium carbonate**

(*i*) It is used for softening hard water.

(*ii*) It is used for washing purposes in laundary.

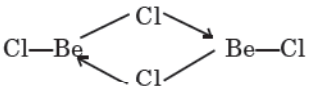
(*c*) **Quick lime**

(*i*) It is used in the manufacture of sodium carbonate from caustic soda.

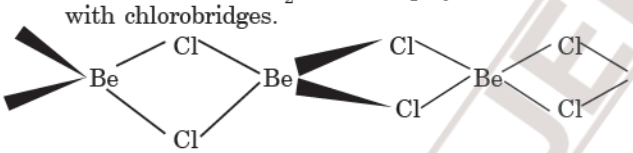
(*ii*) It is used as a flux in metallurgy.

Q.19. Draw the structures of (*i*) $BeCl_2$ (vapour) and (*ii*) $BeCl_2$(solid).

Ans. In vapour state, $BeCl_2$ exists as dimer



In solid state, $BeCl_2$ exists as polymeric structure with chlorobridges.



Q.20. The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

Ans. Sodium and potassium have large size as compared to magnesium and calcium. Therefore, the lattice enthalpies of hydroxides and carbonates of sodium and potassium are much lower than those of hydroxides and carbonates of magnesium and calcium. As a result, the hydroxides and carbonates of sodium and potassium are easily soluble in water whereas the corresponding salts of magnesium and calcium are sparingly soluble in water.

Q.21. Describe the importance of the following : (*i*) limestone (*ii*) cement (*iii*) plaster of paris.

Ans. (*i*) **Limestone**. It is used as a building material in the form of marble. It is used in the preparation of quick lime and as a raw material for the manufacture of sodium carbonate in Solvay process. It is also used as a constituent of tooth paste and filler in cosmetics.

(*ii*) **Cement.** It is an important construction material. It is used in concrete and reinforced concrete, in plastering and in the construction of buildings, bridges, dams, etc.

(*iii*) **Plaster of Paris.** It is used in building industry as well as in plasters. It is used for making statues, models and other decorative materials. It is used in surgical bandages known as plasters for immoblising the fractured bases in the body.

Q.22. Why are lithium salts commonly hydrated and those of the other alkali metal ions usually anhydrous?

Ans. Because of smallest size of Li^+ ion among alkali metal ions, it can polarize water molecules more easily than other alkali metal ions. Therefore, lithium salts get bonded to water of crystallisation. For example, lithium chloride exists as $LiCl.2H_2O$.

Q.23. Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone?

Ans. *Refer Conceptual Questions,* 1 *Q. 12. (Page 19)*

Q. 24. Explain the significance of sodium, potassium, magnesium and calcium in biological fluids.

Ans. *Refer Text page 11–12.*

Q.25. What happens when

(*i*) sodium metal is dropped in water?

(*ii*) sodium metal is heated in free supply of air ?

(*iii*) sodium peroxide dissolves in water?

Ans. (*i*) When sodium metal is dropped in water, hydrogen gas is evolved which catches fire due to exothermic nature of the reaction.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2$$

(*ii*) Sodium peroxide and sodium oxide is formed.

$$2Na(s) + \frac{1}{2}O_2(g) \longrightarrow \underset{\text{(Minor product)}}{Na_2O(s)}$$

$$Na_2O(s) + 1/2O_2(g) \longrightarrow \underset{\text{(Major product)}}{Na_2O_2(s)}$$

(*iii*) When sodium peroxide is dissolved in water, hydrogen peroxide is formed.

$$Na_2O_2(s) + 2H_2O(l) \longrightarrow 2NaOH\ (aq) + H_2O_2(l)$$

Q.26. Comment on each of the following observations:

(*a*) The mobilities of the alkali metal ions in aqueous solution are

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

(*b*) Lithium is the only alkali metal to form a nitride directly.

(*c*) E° for $M^{2+}(aq) + 2e^- \rightarrow M(s)$ (where M = Ca, Sr or Ba) is nearly constant.

Ans. (*a*) The alkali metal ions are highly hydrated. The smaller the size of the ion, the greater is the degree of hydration. Thus, Li^+ ion gets much more hydrated than Na^+ ion which is more hydrated than K^+ ion and so on. Therefore, the extent of hydration decreases from Li^+ to Cs^+. As a result of larger hydration of Li^+ ion than Na^+ ion the effective size of Li^+ ion is more than that of Na^+ ion and ionic radii in water decrease as:

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

Therefore, the mobility of Li^+ ion is slowest and that of Cs^+ ion is maximum. Thus, mobility of ions in water increases as:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

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(*b*) *Refer Conceptual Questions* 1, *Q. 13 (Page 19).*

(*c*) E° value of $M^{2+}/M(s)$ electrode depends upon three factors:

(*i*) enthalpy of vaporisation

(*ii*) ionization enthalpy and

(*iii*) enthalpy of hydration. The combined effect of these factors is approximately the same for Ca, Sr and Ba so that their electrode potentials are nearly same.

Q. 27. State as to why

(*a*) a solution of Na_2CO_3 is alkaline?

(*b*) alkali metals are prepared by electrolysis of their fused chlorides?

(*c*) sodium is found to be more useful than potassium?

Ans. (*a*) *Refer Conceptual Questions* 1 *Q. 14. (Page 19)*

(*b*) The discharge potentials of alkali metals are much higher than that of hydrogen and therefore, when the aqueous solutions of alkali metal chlorides are subjected to electrolysis, H_2 is evolved preferably than the alkali metal at the cathode. Therefore, to prepare alkali metals, electrolysis of their fused chlorides is carried out.

(*c*) Sodium ions are found primarily in the blood plasma and in the interstitial fluid which surrounds the cells. On the other hand, potassium ions are present within the cell fluids. Sodium ions help in the transmission of nerve signals, regulating the flow of water across cell membranes and in the transport of sugars and amino acids in the cells. Thus, sodium is more useful than potassium.

Q. 28. Write balanced equations for reactions between

(*a*) Na_2O_2 and water

(*b*) KO_2 and water

(*c*) Na_2O and CO_2.

Ans. *Refer Solved Example* 10. (*Page 18*)

Q. 29. How would you explain the following observations?

(*i*) BeO is almost insoluble but $BeSO_4$ is soluble in water,

(*ii*) BaO is soluble but $BaSO_4$ is insoluble in water,

(*iii*) LiI is more soluble than KI in ethanol.

Ans. (*i*) BeO is insoluble in water because of its high lattice enthalpy. It is also covalent in nature and therefore, insoluble in water. On the other hand, $BeSO_4$ is ionic. Its hydration enthalpy is much more than its lattice enthalpy and hence it is soluble in water.

(*ii*) Both BaO and $BaSO_4$ are ionic compounds. However, the size of O^{2-} ion is much smaller than that of the SO_4^{2-} ion. Since a bigger anion stabilizes a bigger cation more than a smaller cation stabilizes a bigger anion, therefore, the lattice enthalpy of BaO is smaller than $BaSO_4$. Therefore, BaO is soluble while $BaSO_4$ is insoluble in water.

(*iii*) Li^+ is smaller in size than K^+ ion. Therefore, according to Fazan rules, Li^+ ion can polarize bigger I^- ion to a greater extent than K^+ ion. As a result, LiI is more covalent than KI and hence is more soluble in organic solvents like ethanol.

Q. 30. Which of the alkali metal is having least melting point?

(*a*) Na (*b*) K (*c*) Rb (*d*) Cs

Ans. (*d*) With increase in size, the strength of metallic bonding decreases and therefore, melting point also decreases.

Q. 31. Which one of the following alkali metals gives hydrated salts?

(*a*) Li (*b*) Na (c) K (*d*) Cs

Ans. (*a*) Li^+ being the smallest has highest charge density and hence maximum hydrated.

Q.32. Which one of the alkaline earth metal carbonates is thermally the most stable?

(*a*) $MgCO_3$ (*b*) $CaCO_3$ (*c*) $SrCO_3$ (*d*) $BaCO_3$

Ans. (*d*) As the electropositive character of alkaline earth metals increases down the group, their thermal stability increases. Hence $BaCO_3$ is the most stable.

NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 56*

Short Answer Questions *carrying 2 or 3 marks*

Q. 1. How do you account for the strong reducing power of lithium in aqueous solution ?

Ans. Lithium has most negative electrode potential (–3.04V) among alkali metals and hence it is the strongest reducing agent. This is mainly due to very high enthalpy of hydration in its aqueous solution. For reasons, *Refer text page 10-11.*

Q. 2. When heated in air, the alkali metals form various oxides. Mention the oxides formed by Li, Na and K.

Subjective Questions

Ans. Lithium forms only oxide (Li_2O), sodium forms mainly peroxide (Na_2O_2) and potassium forms superoxide (KO_2). *Refer text page 5-6.*

Q. 3. Complete the following reactions

(*i*) $O_2^{2-} + H_2O \longrightarrow$

(*ii*) $O_2^- + H_2O \longrightarrow$

Ans. (*i*) $O_2^{2-} + 2H_2O \longrightarrow 2OH^- + H_2O_2$

(*ii*) $2O_2^- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$

Q. 4. Lithium resembles magnesium in some of its properties. Mention two such properties and give reasons for this resemblance.

Ans. *Refer diagonal relationship, page 10.*

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Q. 5. Name an element from Group 2 which forms an amphoteric oxide and a water soluble sulphate.

Ans. Beryllium forms amphoteric oxide, BeO. It reacts with acids as well as bases :

$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$ (basic nature)

$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$ (acidic nature)

It also forms highly soluble $BeSO_4$.

Q. 6. Discuss the trend of the following :

(*i*) Thermal stability of carbonates of Group 2 elements.

(*ii*) The solubility and the nature of oxides of Group 2 elements.

Ans. (*i*) The stability of carbonates of Group 2 elements increases down the group.

(*ii*) All the elements of Group 2 form oxides (MO). The solubility of these increases down the group. Among the oxides, BeO is amphoteric and other oxides are basic in nature. *Refer text page 25.*

Q. 7. Why are $BeSO_4$ and $MgSO_4$ readily soluble in water while $CaSO_4$, $SrSO_4$ and $BaSO_4$ are insoluble?

Ans. Th hydration enthalpies of $BeSO_4$ and $MgSO_4$ are quite high because of small size of Be^{2+} and Mg^{2+} ions. These hydration enthalpy values are higher than their corresponding lattice enthalpies and therefore, $BeSO_4$ and $MgSO_4$ are highly soluble in water. However, hydration enthalpies of $CaSO_4$, $SrSO_4$ and $BaSO_4$ are not very high as compared to lattice enthalpies and hence these are insoluble in water.

Q. 8. All compounds of alkali metals are easily soluble in water but lithium compounds are more soluble in organic solvents. Explain.

Ans. Lithium compounds have covalent character and therefore, more soluble in organic solvents. The other alkali metal compounds are ionic in nature and are soluble in water.

Q. 9. In the Solvay process, can we obtain sodium carbonate directly by treating the solution containing $(NH_4)_2CO_3$ with sodium chloride? Explain.

Ans. In Solvay process, we cannot obtain directly sodium carbonate by treating the solution containing $(NH_4)_2CO_3$ with NaCl because both Na_2CO_3 and NH_4Cl are highly soluble and equilibrium will not shift in the forward direction.

$(NH_4)_2CO_3 + 2NaCl \rightleftharpoons Na_2CO_3 + 2NH_4Cl$

Q. 10. Write Lewis structure of O_2^- ion and find out oxidation state of each oxygen atom? What is the average oxidation state of oxygen in this ion?

Ans. Lewis structure is $:\dot{\underset{\cdot\cdot}{O}} - \dot{\underset{\cdot\cdot}{O}}:^-$

Since O having no charge on it has six electrons, its O.N. is zero. The O.N. of oxygen carrying –ve charge has seven electrons and hence its O.N. is –1. The average O.N. of each O atom is $\frac{1}{2}(0-1) = -1/2$

Q. 11. Why do beryllium and magnesium not impart colour to the flame in the flame test ?

Ans. *Refer NCERT Qs. Q. 11.*

Q. 12. What is the structure of $BeCl_2$ molecule in gaseous and solid state?

Ans. *Refer Text and Fig. 5 and 6.*

Long Answer Questions *Carrying 5 marks*

Q. 13. The *s*-block elements are characterised by their larger atomic sizes, lower ionisation enthalpies, invariable +1 oxidation state and solubilities of their oxosalts. In the light of these features describe the nature of their oxides, halides and oxosalts.

Ans. *Refer Text (Page 8).*

Q. 14. Present a comparative account of the alkali and alkaline earth metals with respect to the following characteristics :

(*i*) Tendency to form ionic/covalent compounds

(*ii*) Nature of oxides and their solubility in water

(*iii*) Formation of oxosalts

(*iv*) Solubility of oxosalts

(*v*) Thermal stability of oxosalts

Ans. *Refer Text (Page 7-21).*

Q. 15. When a metal of group 1 was dissolved in liquid ammonia, the following observations were obtained :

(*i*) Blue solution was obtained initially.

(*ii*) On concentrating the solution, blue colour changed to bronze colour.

How do you account for the blue colour of the solution ? Give the name of the product formed on keeping the solution for some time.

Ans. *Refer Text page 6.*

Q. 16. The stability of peroxide and superoxide of alkali metals increase as we go down the group. Explain giving reason.

Ans. *Refer Text page 5.*

Q. 17. When water is added to compound (A) of calcium, solution of compound (B) is formed. When carbon dioxide is passed into the solution, it turns milky due to the formation of compound (C). If excess of carbon dioxide is passed into the solution milkiness disappears due to the formation of compound (D). Identify the compounds A, B, C and D. Explain why the milkiness disappears in the last step.

Ans. When CO_2 gas is passed through solution of compound B, it turns milky, therefore, solution of compound B is $Ca(OH)_2$.

The milkiness is due to the formation of $CaCO_3$(C). Since compound B is obtained by dissolving

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compound (A) in water, compound A must be quick lime, CaO. The reactions are :

$$\underset{\text{Calcium oxide (A)}}{CaO} + H_2O \longrightarrow \underset{\text{Lime water (B)}}{Ca(OH)_2}$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{Calcium carbonate (C) (Milkiness)}}{CaCO_3} + H_2O$$

Milkiness disappears on passing excess CO_2 because of the formation of soluble calcium bicarbonate.

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{\text{Soluble (D) Milkiness disappears}}{Ca(HCO_3)_2}$$

Q. 18. Lithium hydride can be used to prepare other useful hydrides. Beryllium hydride is one of them. Suggest a route for the preparation of beryllium hydride starting from lithium hydride. Write chemical equations involved in the process.

Ans.
$$8LiH + Al_2Cl_6 \longrightarrow 2LiAlH_4 + 6LiCl$$
$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

Q. 19. An element of group 2 forms covalent oxide which is amphoteric in nature and dissolves in water to give an amphoteric hydroxide. Identify the element and write chemical reactions of the hydroxide of the element with an alkali and an acid.

Ans. The element is Be and its covalent oxide is BeO. Its reaction with acids and bases are :

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH \xrightarrow{\text{Heat}} \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2O$$

Q. 20. Ions of an element of group 1 participate in the transmission of nerve signals and transport of sugars and aminoacids into cells. This element imparts yellow colour to the flame in flame test and forms an oxide and a peroxide with oxygen. Identify the element and write chemical reaction to show the formation of its peroxide. Why does the element impart colour to the flame ?

Ans. Since the alkali metal imparts yellow colour in the flame test, it must be sodium.

It reacts with O_2 to form sodium peroxide and sodium oxide.

$$4Na + O_2 \xrightarrow{\text{Heat}} \underset{\text{Sodium oxide}}{2Na_2O}$$

$$2Na + O_2 \longrightarrow \underset{\text{Sodium peroxide}}{Na_2O_2}$$

$$2Na_2O + O_2 \xrightarrow{\text{Heat}} \underset{\text{Sodium peroxide}}{2Na_2O_2}$$

So mainly sodium peroxide is formed.

Why does sodium impart yellow colour to the flame ? The ionization enthalpy of sodium is low. When sodium metal or its salt is heated in Bunsen flame, its outermost electron gets excited to higher energy levels by absorption of energy. When the excited electron returns to the ground state, it emits the extra energy which falls in yellow region of the visible spectrum. Therefore, sodium imparts yellow colour to the flame.

QUICK MEMORY TEST

A. Say True or False

1. Sodium is stronger reducing agent than magnesium.
2. The solubilities of metal carbonates in water decreases down the family.
3. Chlorophyll is an important complex of calcium.
4. Potassium has higher density than sodium.
5. Beryllium and magnesium donot give characteristic colour to the flame.
6. LiF is almost insoluble in water whereas LiCl is soluble.
7. Lithium floats on water without any apparent reaction with it.
8. KO_2 is diamagnetic oxide.
9. Sodium nitrate on heating gives nitrogen dioxide and oxygen.
10. Beryllium resembles more with aluminium than with magnesium.

B. Complete the missing links

1. The radioactive alkali metal is .....
2. Lithium shows diagonal relationship with .....
3. The bicarbonate of alkali metal which does not exist in the solid state is .....
4. Oxidation state of sodium in sodium peroxide is .....
5. Lithium reacts readily with nitrogen to form .....
6. Solvay process is used for the manufacture of .....
7. Alkali metals dissolve in liquid ammonia to form ..... coloured solutions.
8. The reactivity of alkali metals ..... from Li to Cs.
9. ..... gives golden yellow colour to the flame.
10. Plaster of paris is obtained by heating .....

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C. Choose the correct alternative

1. Lithium forms only *oxide / peroxide*.
2. Among the peroxides of alkaline earth metals, MgO_2 is the *least / most* stable.
3. The hydration energy of Li^+ ion is *more / less* than that of Na^+ ion.
4. $Mg(OH)_2$ is *less / more* basic than $Ca(OH)_2$.
5. K_2CO_3 *can / cannot* be prepared by Solvay process like Na_2CO_3.
6. Among alkali metals cesium can show photoelectric effect to the *maximum / minimum* extent.
7. The superoxide ion is *diamagnetic / paramagnetic*.
8. The alkali metal hydrides behave as strong *reducing / oxidising* agents.
9. Among the alkali metal halides MF, MCl, MBr and MI, covalent character *increases / decreases*.
10. Alkali metals can be stored in *benzene / ethanol*.

Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. True
3. **False :** Chlorophyll is a complex of magnesium.
4. **False :** Potassium has lower density than sodium.
5. True
6. True
7. True
8. **False :** KO_2 is paramagnetic.
9. **False :** Sodium nitrate decomposes as :

$$2NaNO_3 \xrightarrow{Heat} 2NaNO_2 + O_2$$

10. True.

B. Complete the missing links

1. francium
2. magnesium
3. $LiHCO_3$
4. +1
5. Lithium nitride (Li_3N)
6. $Na_2CO_3 \cdot 10H_2O$ (sodium carbonate)
7. blue
8. decreases
9. sodium
10. gypsum

C. Choose the correct alternative

1. oxide
2. most
3. more
4. less
5. cannot
6. maximum
7. paramagnetic
8. reducing
9. increases
10. benzene

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Name the element which is invariably bivalent and whose oxide is soluble in excess of NaOH and its dipositive ion has noble gas configuration.

Ans. Beryllium BeO dissolves in NaOH to form sodium beryllate.

$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O.$$

Q. 2. $BeCl_2$ gives an acidic solution when dissolved in water. Why ?

Ans. $BeCl_2$ gets hydrolysed in water forming H^+ ions and therefore, the solution is acidic.

$$BeCl_2\,(s) + 2H_2O \longrightarrow Be(OH)_2 + 2H^+ + 2Cl^-$$

Q. 3. Salts of alkaline earth metals are colourless and diamagnetic. Explain.

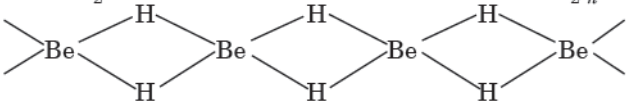
Ans. Alkaline earth metals form dipositive ions in their salts. These dipositive ions have noble gas configurations with no unpaired electrons. Therefore, these compounds are colourless and diamagnetic.

Q. 4. LiI_3 is less stable than CsI_3. Why?

Ans. This is due to lattice energy effects. The large cation stabilizes a large anion in its lattice. Therefore, CsI_3 is more stable because Cs^+ being large cation can stabilize large I_3^- ion.

Q. 5. Describe the difference in structure between CaH_2 and BeH_2.

Ans. CaH_2 is an ionic solid consisting of Ca^{2+} and H^- ions having slightly distorted *hcp* arrangement. On the other hand, BeH_2 has polymeric bridged like structure $(BeH_2)_n$.



Q. 6. LiF is insoluble in water whereas other alkali metal fluorides are soluble.

Ans. Both Li^+ and F^- ions have small size and therefore, LiF has high lattice energy. Although the hydration energy of LiF is also high but, it is less than lattice energy (hydration energy of LiF = –1034 kJ, lattice energy = –1045 kJ). Therefore, it is insoluble.

On the other hand, all other alkali metal fluorides have lower lattice energies than corresponding hydration energies and therefore, these are soluble.

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Q.7. Why are alkali metals soft and have low melting points ?

Ans. Alkali metals have only one valence electron per metal atom. As a result, the binding energy of alkali metal ions in the close-packed metal lattices are weak. Therefore, these are soft and have low melting points.

Q.8. LiH, LiF and Li_3N show exceptional thermal stabilities. Explain.

Ans. Li^+ is very small in size. Therefore, its salts with small anions such as F^-, H^- and N^{3-} are exceptionally stable due to their high lattice energies.

Q.9. When burnt in air, lithium forms normal oxide, Na the peroxide and K the superoxide. Why ?

Ans. Li^+ is very small in size and has strong field around it. It can stabilize only small sized oxide O^{2-} ion and therefore, forms only Li_2O. It cannot stabilize other large anions such as peroxide (O_2^{2-}) and superoxide (O_2^-).

Na^+ being larger in size can stabilize large peroxide ion (O_2^{2-}) and therefore, forms peroxides.

K^+ being large can also stabilize large superoxide ion (O_2^-) forming superoxides.

Q.10. Li_2CO_3 is unstable while all other alkali metal carbonates are relatively stable. Explain.

Ans. Li^+ ion being small in size, cannot stabilize large CO_3^{2-} ion and therefore, Li_2CO_3 is unstable. Other alkali metal ions are large in size and can easily stabilize large CO_3^{2-} ions. This is because of lattice energy effects.

Q.11. Which out of the following and why can be used to store an alkali metal ?

H_2O, C_2H_5OH, Benzene

Ans. Benzene can be used to store an alkali metal because other substances react with alkali metals as :

$$Na + H_2O \longrightarrow NaOH + \tfrac{1}{2}H_2$$
$$Na + C_2H_5OH \longrightarrow C_2H_5ONa + \tfrac{1}{2}H_2$$

Q.12. Mg^{2+} is much more hydrated than Na^+. Why?

Ans. The extent of hydration depends upon the charge density (charge/size). Mg^{2+} ion is smaller in size than Na^+ and has twice the charge than Na. Therefore, its charge density is high and hence is extensively hydrated.

Q.13. Explain the following :

(*a*) $Be(OH)_2$ dissolves in sodium hydroxide but $Mg(OH)_2$ does not.

(*b*) Beryllium halides are polymeric in nature.

Ans. (*a*) $Be(OH)_2$ is amphoteric and therefore, it dissolves in NaOH forming sodium beryllate :

$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$

On the other hand, $Mg(OH)_2$ is basic and does not dissolve in NaOH.

(*b*) The beryllium halides are electron deficient covalent compounds because they have only four electrons in the valence shell. Therefore, to complete their octets, they undergo polymerisation.

Q.14. Mg_3N_2 when reacted with water gives off ammonia but HCl is not obtained from $MgCl_2$ on reaction with water at room temperature. Explain.

Ans. Mg_3N_2 is a salt of a strong base $Mg(OH)_2$ and a weak acid NH_3 and therefore, gets hydrolysed giving NH_3. On the other hand, $MgCl_2$ is a salt of strong acid HCl and a strong base $Mg(OH)_2$ and therefore, does not undergo hydrolysis to give HCl.

Q.15. LiH is more stable than NaH. Explain.

Ans. Both Li^+ and H^- have small size and their combination has high lattice energy. Therefore, LiH is stable as compared with NaH.

Q.16. Sodium fire in the laboratory should not be extinguished by pouring water. Why ?

Ans. Sodium reacts violently with water producing hydrogen which also catches fire. Therefore, the fire increases on adding water instead of getting extinguished. Hence, water should not be used for extinguishing sodium fire. It can be extinguished by pyrene (CCl_4).

Q.17. Can you dissolve sodium hydride in water ?

Ans. No, sodium hydride cannot be dissolved in water because it gets hydrolysed with brisk evolution of hydrogen gas.

$$NaH + H_2O \longrightarrow H_2 + NaOH$$

Q.18. The crystalline salts of alkaline earth metals contain more water of crystallization than the corresponding alkali metal salts. Explain.

Ans. Alkaline earth metals have smaller size and higher nuclear charge than alkali metals. Therefore, alkaline earth metals have a higher tendency to attract water molecules and hence contain more water of crystallisation molecules than alkali metals. For example, $MgCl_2.6H_2O$. However, among alkali metals only lithium because of its small size forms hydrated salts such as $LiCl.2H_2O$.

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Name the groups which constitute *s*-block elements.
2. Write the general configuration of *s*-block elements.
3. What is the position of Na and K in the order of abundance among elements ?
4. Why does the basic character of hydroxides of alkali metals increase down the group ?
5. What is the chemical formula of Plaster of Paris ? Give its one use.
6. What is the cause of diagonal relationship among elements ?
7. How does the solubility of hydroxides of alkaline earth metals vary as we move down the group ?
8. Give two main reasons for the differences of properties of Li and Na.

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9. Give the chemical formula of limestone and Plaster of Paris.
10. Alkali and alkaline earth metals cannot be obtained by chemical reduction method. Explain.
11. Name the compound which can be obtained by Solvay's process.
12. Why do we store sodium metal in kerosene oil and not in water ?
13. What is quicklime ? What happens when we add water to quicklime ?
14. What is dead burnt plaster ?
15. Why cannot sodium be prepared by the electrolysis of its aqueous solution ?
16. Why does lithium form monoxide while sodium form peroxides ?
17. How does the basic character of hydroxides of alkali metals vary down the group ?
18. Compare the action of heat on $LiNO_3$ and $NaNO_3$.
19. Which out of Li or Na forms nitrides ? Why ?
20. Give two uses of Na_2CO_3.
21. Name radioactive elements of group 1 and 2.
22. Why does magnesium not give flame colouration ?
23. Which is the most abundant element among alkaline earth metals ?
24. Which out of Na^+ or K^+ ion has higher concentration within the cells ?
25. Which out of $MgSO_4$ or $BaSO_4$ is more soluble in water?

Short Answer Questions *carrying 2 or 3 marks*

1. What are the common physical and chemical features of alkali metals?
2. Why do not Be and Mg give characteristic flame colouration while others do ?
3. Discuss the general characteristics and gradation in properties of alkaline earth metals.
4. How do the following properties vary among alkali metals ?
   (*i*) Atomic radius
   (*ii*) Ionisation energy
   (*iii*) Metallic character.
5. Name the alkali metals which form superoxides when heated in excess of air. ***N.C.E.R.T.***
6. Alkali metals are good reducing agents. Explain.
7. Lithium differs from other alkali metals. Explain with examples.
8. Compare the alkali metals and alkaline earth metals with respect to
   (*i*) ionisation enthalpy
   (*ii*) basicity of oxides
   (*iii*) solubility of hydroxides
9. Explain the extraction of sodium from sodium chloride.
10. Give the chemical formulae of the following ores :
    (*i*) Dolomite (*ii*) Gypsum
    (*iii*) Epsom salt (*iv*) Carnallite
11. Name the chief factor responsible for the anomalous behaviour of lithium. ***N.C.E.R.T.***
12. Why is it necessary to add gypsum in the final stages of the preparation of cement ?
13. Describe a method for the preparation of quicklime. What happens when water is poured over quicklime ?
14. Differentiate between
    (*i*) Quicklime (*ii*) Lime water
    (*iii*) Slaked lime
15. Contrast the action of heat on the following and explain your answer : ***N.C.E.R.T.***
    (*i*) Na_2CO_3 and $CaCO_3$
    (*ii*) $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$
    (*iii*) $Ca(NO_3)_2$ and $NaNO_3$
16. State as to why ? ***N.C.E.R.T.***
    (*i*) Sodium is found more useful than potassium
    (*ii*) Solution of Na_2CO_3 is alkaline
    (*iii*) Alkali metals are prepared by the electrolysis of their fused chlorides
17. In what ways, lithium shows similarities to magnesium in its chemical behaviour ?
18. State the effect of heat on
    (*i*) gypsum (*ii*) limestone (*iii*) epsom salt. ***N.C.E.R.T.***
19. What is cement ? Give the chemistry of manufacture of cement.
20. Write three general characteristics of elements of *s*-block of the periodic table which distinguish them from the element of the other blocks.
21. What happens when
    (*i*) Sodium metal is dropped in water ?
    (*ii*) Sodium metal is heated in free supply of air ?
    (*iii*) Sodium peroxide dissolves in water ?
22. Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals :
    (*i*) Nitrates (*ii*) Carbonates
    (*iii*) Sulphates. ***N.C.E.R.T.***
23. Describe the principle involved in the electrolysis of molten sodium chloride.
24. Explain the chemistry of Down's process for the extraction of sodium.
25. Describe the preparation of each of the following starting with limestone :
    (*i*) Plaster of paris (*ii*) Slaked lime.
26. In what way does lithium show similarities to magnesium in its chemical behaviour ?
27. Account for the thermal stability and solubility of oxosalts of alkaline earth metals.
28. Beryllium exhibits some similarities with aluminium. Point out four such properties.
29. Explain thetrends in solubility of sulphates and hydroxides of alkaline earth metals.
30. Draw the structure of
    (*i*) $BeCl_2$ (vapour) (*ii*) $BeCl_2$ (*s*) ***N.C.E.R.T.***
31. Starting with sodium chloride how would you proceed to prepare (state the steps only)
    (*i*) sodium metal (*ii*) sodium hydroxide
    (*iii*) sodium peroxide (*iv*) sodium carbonate.

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32. "The chemistry of beryllium is not essentially ionic". Justify the statement by making a reference to the nature of oxide, chloride and fluoride of beryllium.

33. Why does the following reaction :

$$\gtrless C—Cl + MF \longrightarrow \gtrless C—F + MCl$$

proceed better with KF than with NaF ? ***N.C.E.R.T.***

34. Why is it difficult to extract alkali metals by usual methods ?

35. Give three uses each of lithium and sodium.

36. Give the chemistry of Solvay process for the manufacture of Na_2CO_3.

37. The second ionization energy of alkaline earth metals is greater than the first ionisation energy, yet they prefer to form +2 ions. Explain.

38. Explain the following properties of alkaline earth metals :
(*i*) Formation of oxides
(*ii*) Formation of hydroxides.

39. Give one method of preparation and two uses of each of the following :
(*i*) Slaked lime (*ii*) Limestone
(*iii*) Plaster of Paris.

40. Describe the importance of the following :
(*i*) Cement (*ii*) Plaster of Paris
(*iii*) Limestone.

41. Explain the following :
(*i*) The mobilities of the alkali metal ions in aqueous solutions are :
$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$
(*ii*) Lithium is the only alkali metal to form nitride directly
(*iii*) LiF is least soluble among the fluorides of alkali metals.
(*iv*) E° for $M^{2+}(aq) + 2e^- \longrightarrow M(s)$ (where M = Ca, Sr or Ba) is nearly constant. ***N.C.E.R.T.***

42. What happens when
(*i*) calcium nitrate is heated
(*ii*) chlorine reacts with slaked lime
(*iii*) quicklime is heated with silica
(*iv*) magnesium is burnt in air.

43. Give an account of industrial uses of lime and limestone.

44. The alkali metals follow the noble gases in their atomic structures. What properties of these metals can be predicted from this information.

45. Give the chemistry of extraction of magnesium by Down's process ?

46. Describe three industrial uses of caustic soda. Describe one method for the manufacture of sodium hydroxide. What happens when sodium hydroxide reacts with
(*i*) SiO_2 (*ii*) CO_2 (*iii*) Al metal

47. Commercial aluminium always contains some magnesium. Name two such alloys of aluminium. What properties are imparted by the addition of magnesium to these alloys ?

48. List four properties of Li in which it differs from rest of the family members.

49. List four properties of Be in which Be differs from rest of the family members.

50. Give two important uses of each of the following :
(*i*) Quicklime (*ii*) Caustic soda
(*iii*) Sodium carbonate.

51. Lithium forms only monoxide, sodium peroxide and potassium superoxide. Explain.

52. Discuss the various reactions that occur in Solvay process.

53. How is Plaster of Paris prepared ?

54. Like lithium in Group 1, beryllium shows anomalous behaviour in Group 2. Write three such properties of beryllium which make it anomalous in the group.

55. 'The chemistry of beryllium is not essentially ionic'. Jusfify the statement by making a reference to the nature of oxide, chloride and fluoride of beryllium.

56. Why is that the *s*-block elements never occur free in nature ? What are their usual modes of occurrence and how are they generally prepared ?

57. When an alkali metal is dissolved in liquid ammonia the solution acquires different colours. Explain the reason for this type of colour change. ***N.C.E.R.T.***

58 Discuss the trend of the following :
(*i*) Thermal stability of carbonates of Group 2 elements.
(*ii*) The solubility and the nature of oxides of Group 2 elements. *(NCERT Exemplar Problem)*

59. What is the structure of $BeCl_2$ molecule in gaseous and solid state ? *(NCERT Exemplar Problem)*

60. All compounds of alkali metals are easily soluble in water but lithium compounds are more soluble in organic solvents. Explain.*(NCERT Exemplar Problem)*

Long Answer Questions *Carrying 5 marks*

1. What are alkali metals ? Explain their occurrence and discuss their important chemical properties.

2. Explain the following properties of alkaline earth metals :
(*i*) Tendency to give characteristic flame colouration
(*ii*) Action with air
(*iii*) Action with water
(*iv*) Thermal stability of sulphates.

3. What is diagonal relationship ? What is its cause ? Discuss any five points to show diagonal relationship between lithium and magnesium.

4. Name the important ores of lithium. Explain its extraction from its ores. Give important properties and uses of lithium.

5. Name the important ores of sodium. How is it extracted from its ores ? Explain important properties and its uses.

6. The first member of each group differs from its congeners. Why ? Discuss by taking a specific example.

7. Describe in detail the manufacture of sodium carbonate by Solvay process. State the principles involve in the process.

8. How does magnesium occur in nature? How is magnessium metal obtained by the electrolysis method?

9. Name a few important uses of the following compounds:
(*i*) Sodium carbonate (*ii*) Epsom salt
(*iii*) Quick lime (*iv*) Plaste of Paris

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10. Describe the preparation of each of the following starting from limestone.
(*i*) Slaked lime (*ii*) Calcium carbide
(*iii*) Plaster of Paris

11. What is cement ? What is its composition ? How is it manufactured ?

12. What are *s*–block elements ? Discuss their occurrence. Compare the following properties of alkali metal and alkaline earth metals :
(*i*) Ionization energy (*ii*) Basicity of oxides
(*iii*) Basicity of hydroxides.

13. What are *s*–block elements ? Compare and contrast the chemistry of group 1 metals with those of group 2 metals with respect to
(*i*) nature of oxides
(*ii*) polarizing power of cations
(*iii*) solubility and thermal stability of carbonates
(*iv*) reactivity and reducing power.

14. Write balanced equations for the reactions between :
(*i*) Na_2O and CO_2 (*ii*) KO_2 and water
(*iii*) $BeO + H_2SO_4$ (*iv*) $Ca(OH)_2 + Cl_2$
(*v*) BeO + NaOH (*vi*) Na_2O_2 and water
(*vii*) $Ca + H_2O$

15. Give a brief account of the following :
(*i*) Blue coloured solutions of alkali metals in liquid ammonia
(*ii*) Tendency to form divalent compounds of alkaline earth metals than monovalent.
(*iii*) Tendency to give flame colours by alkali metals.
(*iv*) Importance of lime and limestone.

16. How would you explain :
(*i*) BeO is insoluble but $BeSO_4$ is soluble in water.
(*ii*) BaO is soluble but $BaSO_4$ is insoluble in water.
(*iii*) LiI is more soluble than KI in ethanol.

17. How do the following properties change on moving from group 1 to Group 2 in the periodic table ?
(*i*) Atomic size (*ii*) Ionization enthalpy
(*iii*) Density (*iv*) Melting point

N.C.E.R.T.

18. State as to why
(*i*) lithium on being heated in air mainly forms the monoxide and not the peroxide.
(*ii*) an aqueous solution of sodium carbonate gives alkaline tests.
(*iii*) sodium is prepared by electrolytic method and not by chemical method.

19. Present a comparative account of the alkali and alkaline earth metals with respect to the following characteristics :
(*i*) Tendency to form ionic/covalent compounds
(*ii*) Nature of oxides and their solubility in water
(*iii*) Formation of oxosalts
(*iv*) Solubility of oxosalts
(*v*) Thermal stability of oxosalts.
(NCERT Exemplar Problem)

Hints & Answers for Revision Exercises

Very Short Answer Questions

2. : [Noble gas] $ns^{1,2}$

3. : Sodium is the 7th and potassium is 8th most abundant element by wt in earth's crust.

7. : increases as we go down the group

9. : $CaCO_3, (CaSO_4).\frac{1}{2}H_2O$

11. : Sodium carbonate

17. : increases down the group

23. : calcium

24. : K^+ ion

25. : $MgSO_4$

Short Answer Questions

21. (*i*) : $2Na + 2H_2O \longrightarrow 2Na^+ + 2OH^- + H_2$
(*ii*) : $2Na + O_2 \longrightarrow Na_2O_2$
(*iii*) : $Na_2O_2 + 2H_2O_2 \longrightarrow 2Na^+ + 2OH^- + H_2O_2$

31. (*i*) : $NaCl \xrightarrow{\text{Electrolysis}} Na^+ + Cl^-$
Molten
At cathode : $Na^+ + e^- \longrightarrow Na(s)$
At anode : $2Cl^- - 2e^- \longrightarrow Cl_2$

(*ii*) : $NaCl\ (aq) \xrightarrow{\text{Electrolysis}} Na^+(aq) + Cl^-(aq)$

$H_2O \longrightarrow H^+ + OH^-$

$Na^+ + e^- \longrightarrow Na$

$Na + Hg \longrightarrow Na/Hg$

$2Na/Hg + 2H_2O \longrightarrow 2NaOH + H_2 + Hg$

(*iii*) : $NaCl \longrightarrow Na^+ + Cl^-$
At cathode : $Na^+ + e^- \longrightarrow Na(s)$
$2Na + O_2 \longrightarrow Na_2O_2$

(*iv*) : $NH_3 + H_2O + CO_2 \longrightarrow (NH_4)HCO_3$
$NaCl + NH_4CO_3 \longrightarrow NaHCO_3 + NH_4Cl$
$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3 + CO_2 + H_2O$

42. (*i*) : $2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$

(*ii*) : $2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$

(*iii*) : $CaO + SiO_2 \xrightarrow{\Delta} CaSiO_3$

(*iv*) : $2Mg + O_2 \longrightarrow 2MgO$
$3Mg + N_2 \longrightarrow Mg_3N_2$

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Competition File

Objective Questions

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Alkali metals

A1. Which of the following is most basic ?
(a) CsOH (b) KOH
(c) LiOH (d) RbOH

A2. Lithium shows diagonal relationship with
(a) Beryllium (b) Magnesium
(c) Calcium (d) Boron

A3. Down's process is used for the extraction of
(a) Na (b) Li
(c) Ba (d) Mg

A4. Carnallite is :
(a) $KCl\,MgCl_2 . 6H_2O$ (b) Na_3AlF_6
(c) $Ca_2B_6O_{11} . 2H_2O$ (d) $Ca_2Mg_2Si_6O_{22}(OH)_2$

A5. Solvay process is used for the manufacture of
(a) NaOH (b) Na_2CO_3
(c) NH_3 (d) NaCl

A6. Which of the following is not an ore of lithium?
(a) Petalite (b) Triphylite
(c) Albite (d) Spodumene

A7. Which of the following is radioactive alkali metal ?
(a) Fr (b) Ra
(c) At (d) Rn

A8. The stability of the following alkali metal chlorides follows the order :
(a) LiCl > KCl > NaCl > CsCl
(b) CsCl > KCl > NaCl > LiCl
(c) NaCl . KCl . LiCl . CsCl
(d) KCl > CsCl > NaCl > LiCl

A9. The metallic lustre exhibited by sodium is explained by
(a) diffusion of sodium ions
(b) oscillation of loose electrons
(c) excitation of free electrons
(d) existence of body centred cubic lattice

A10. On dissolving moderate amount of sodium metal in liquid ammonia at low temperature, which one of the following does not occur ?
(a) Blue coloured solution is obtained
(b) Na^+ ions are formed in the solution
(c) Liquid ammonia becomes good conductor of electricity
(d) liquid ammonia remains diamagnetic.

A11. The correct order of mobility of alkali metal ions in aqueous solution is
(a) $Na^+ > K^+ > Rb^+ > Li^+$
(b) $K^+ > Rb^+ > Na^+ > Li^+$
(c) $Rb^+ > K^+ > Na^+ > Li^+$
(d) $Li^+ > K^+ > Na^+ > Rb^+$ *(C.B.S.E. Med. 2006)*

A12. When sodium burns in excess air, the main product formed is
(a) sodium oxide
(b) sodium peroxide
(c) sodium superoxide
(d) sodium oxide and sodium nitrate

Alkaline earth metals

A13. Which of the following alkaline earth metals does not impart characteristic colour to the flame ?
(a) Be (b) Ca
(c) Ba (d) Sr

A14. Which of the following alkaline earth metal ion has smallest mobility in aqueous solution ?
(a) Mg^{2+} (b) Ca^{2+}
(c) Sr^{2+} (d) Ba^{2+}

A15. Beryllium exhibits diagonal relationship with
(a) Boron (b) Aluminium
(c) Magnesium (d) Silicon

A16. Which of the following is most stable ?
(a) $BeCO_3$ (b) $MgCO_3$
(c) $SrCO_3$ (d) $CaCO_3$

A17. Magnesium is present in
(a) Haemoglobin (b) Chlorophyll
(c) Vitamin B_{12} (d) Ascorbic acid.

A18. Quicklime is :
(a) $Ca(OH)_2$ (b) $CaCO_3$
(c) CaO (d) $CaSO_4$

A19. Slaked lime reacts with chlorine to give
(a) $CaCl_2$ (b) CaO
(c) $CaOCl_2$ (d) $CaCO_3$

A20. The by-product in Solvay ammonia process is
(a) Carbon dioxide (b) Ammonia
(c) Calcium chloride (d) Calcium carbonate

A21. Epsom salt is
(a) $Na_2SO_4.10\,H_2O$ (b) $FeSO_4.7\,H_2O$
(c) $MgSO_4.7\,H_2O$ (d) $MgCl_4.7\,H_2O$

A22. Which of the following has largest solubility in water ?
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Sr(OH)_2$

Answers

A1. (a) **A2.** (b) **A3.** (a) **A4.** (a) **A5.** (b) **A6.** (c) **A7.** (a) **A8.** (a) **A9.** (b) **A10.** (d) **A11.** (c)
A12. (b) **A13.** (a) **A14.** (a) **A15.** (b) **A16.** (c) **A17.** (b) **A18.** (c) **A19.** (c) **A20.** (c) **A21.** (c) **A22.** (c)

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A23. Which of the following is not an ore of magnesium ?
(a) Epsom salt (b) Dolomite
(c) Asbestos (d) Gypsum

A24. Which of the following readily forms nitride ?
(a) K (b) Mg
(c) Ba (d) Ca

A25. Gypsum on heating to 390 K gives
(a) $CaSO_4.2H_2O$ (b) $CaSO_4$
(c) $CaSO_4.\frac{1}{2}H_2O$ (d) SO_3 and CaO

A26. Among the alkaline earth metals, the element forming predominantly covalent compound is
(a) Barium (b) Strontium
(c) Calcium (d) Beryllium

A27. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order :
K_2CO_3(I), $MgCO_3$(II), $CaCO_3$(III), $BeCO_3$(IV)
(a) I < II < III < IV (b) IV < II < III < I
(c) IV < II < I < III (d) II < IV < III < I

A28. Which of the following statements about alkaline earth metals are correct?
1. Hydration enthalpy of Sr^{2+} is greater than that of Be^{2+}
2. $CaCO_3$ decomposes at a higher temperature than $BeCO_3$
3. $Ba(OH)_2$ is a stronger base than $Mg(OH)_2$
4. $SrSO_4$ is less soluble in water than $CaSO_4$.
Select the correct answer using the codes given below:
(a) 4 only (b) 1 and 3
(c) 3 and 4 (d) 3 and 4

Answers

A23. (d) **A24.** (b) **A25.** (c) **A26.** (d) **A27.** (b) **A28.** (d)

B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

AIPMT & Other State Boards' Medical Entrance

B1. The sequence of ionic mobility in aqueous solution is :
(a) $K^+ > Na^+ > Rb^+ > Cs^+$
(b) $Cs^+ > Rb^+ > K^+ > Na^+$
(c) $Rb^+ > K^+ > Cs^+ > Na^+$
(d) $Na^+ > K^+ > Rb^+ > Cs^+$ *(C.B.S.E. Med. 2008)*

B2. The alkali metals form salts like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following order ?
(a) CsH > RbH > KH > NaH > LiH
(b) KH > NaH > LiH > CsH > RbH
(c) NaH > LiH > KH > RbH > CsH
(d) LiH > NaH > KH > RbH > CsH
(C.B.S.E. Med. 2008)

B3. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH?
(a) $SrCl_2$ (b) $BaCl_2$
(c) $MgCl_2$ (d) $CaCl_2$ *(C.B.S.E. Med. 2008)*

B4. In case of alkali metals, the covalent character decreases in the order
(a) MF > MCl > MBr > MI
(b) MF > MCl > MI > MBr
(c) MI > MBr > MCl > MF
(d) MCl > MI > MBr > MF *(C.B.S.E. PMT 2009)*

B5. Which of the following oxides is not expected to react with sodium hydroxide ?
(a) CaO (b) SiO_2
(c) BeO (d) B_2O_3 *(C.B.S.E. PMT 2009)*

B6. Which of the following does not react with water even under red hot condition ?
(a) Na (b) Be (c) Ca (d) K
(e) Sr *(Kerala PMT 2009)*

B7. Which of the following on thermal decomposition yields a basic as well as acidic oxide?
(a) $KClO_3$ (b) Na_2CO_3
(c) $NaNO_3$ (d) $CaCO_3$
(e) NH_4NO_3 *(Kerala PMT 2008)*

B8. Which among the following is kinetically inert towards water ?
(a) Na (b) Be
(c) Ca (d) K (e) Sr *(Kerala PMT 2010)*

B9. The property of alkaline earth metals that increases with their atomic number is
(a) Electronegativity
(b) Solubility of their hydroxides in water
(c) Solubility of their sulphates in water
(d) Ionization enthalpy *(C.B.S.E. Med. 2010)*

B10. Which of the following alkaline earth metal sulphates has hydration enthalpy higher than the lattice enthalpy ?
(a) $SrSO_4$ (b) $CaSO_4$
(c) $BeSO_4$ (d) $BaSO_4$ *(C.B.S.E. Med. 2010)*

B11. The increasing order of the density of alkali metals is
(a) Li < K < Na < Rb < Cs
(b) Li < Na < K < Rb < Cs
(c) Cs < Rb < Na < K < Li
(d) Cs < Rb < K < Na < Li
(e) Li < Na < Rb < K < Cs *(Kerala PMT 2011)*

B12. The alkali metal halide that is soluble in pyridine is
(a) NaCl (b) LiCl (c) KCl (d) CsI
(e) NaBr *(Kerala PMT 2011)*

Answers

B1. (b) **B2.** (d) **B3.** (b) **B4.** (c) **B5.** (a) **B6.** (e) **B7.** (d) **B8.** (b) **B9.** (b) **B10.** (c)
B11. (a) **B12.** (b)

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B13. When Br_2 is treated with aqueous solutions of NaF, NaCl and NaI separately ?
(*a*) F_2, Cl_2 and I_2 are liberated
(*b*) only F_2 and Cl_2 are liberated
(*c*) only I_2 is liberated
(*d*) only Cl_2 is liberated
(*e*) only Cl_2 and I_2 are liberated *(Kerala PMT 2011)*

B14. Which one of the following is present as an active ingredient in bleaching powder for bleaching action ?
(*a*) $CaOCl_2$ (*b*) $Ca(OCl)_2$
(*c*) CaO_2Cl (*d*) $CaCl_2$ *(AIPMT 2011)*

B15. Which of the following compound has the lowest melting point ?
(*a*) $CaCl_2$ (*b*) $CaBr_2$
(*c*) CaI_2 (*d*) CaF_2 *(AI PMT 2011)*

B16. Choose the incorrect statement in the following
(*a*) BeO is almost insoluble but $BeSO_4$ is soluble in water.
(*b*) BaO is soluble but $BaSO_4$ is insoluble in water.
(*c*) LiI is more soluble than KI in ethanol
(*d*) Both Li and Mg form solid hydrogen carbonates.
(*e*) Both LiCl and $MgCl_2$ are deliquescent.
(Kerala P.M.T. 2012)

B17. The correct formula of plaster of Paris is
(*a*) $CaSO_4.2H_2O$ (*b*) $CaSO_4.H_2O$
(*c*) $Ca_2SiO_4.2H_2O$ (*d*) $Ca_3SiO_5.H_2O$
(*e*) $CaSO_4.\frac{1}{2}H_2O$ *(Kerala P.M.T. 2012)*

B18. Which one of the alkali metals, forms only, the normal oxide, M_2O on heating in air ?
(*a*) Rb (*b*) K
(*c*) Li (*d*) Na *(A.I.P.M.T. 2012)*

B19. Which of the following is the weakest base?
(*a*) $Ca(OH)_2$ (*b*) KOH
(*c*) Li(OH) (*d*) $Sr(OH)_2$ *(A.M.U. Med. 2013)*

B20. Which one of the following is a strong base?
(*a*) NaOH (*b*) KOH
(*c*) $Ca(OH)_2$ (*d*) $Mg(OH)_2$ *(A.M.U. Med. 2013)*

B21. The element responsible for the neuromuscular function in the body is
(*a*) calcium (*b*) magnesium
(*c*) potassium (*d*) sodium
(*e*) manganese *(Kerala P.M.T. 2015)*

B22. The salt of an alkali metal gives yellow colour in the flame test. Also its aqueous solution gives an insoluble white precipitate with barium chloride in acidic medium. The salt is
(*a*) NaCl (*b*) K_2SO_4
(*c*) Na_2SO_4 (*d*) Li_2SO_4
(*e*) $NaNO_3$ *(Kerala P.M.T. 2015)*

B22. Solubility of the alkaline earth metal sulphates in water decreases in the sequence:
(*a*) Sr > Ca > Mg > Ba
(*b*) Ba > Mg > Sr > Ca
(*c*) Mg > Ca > Sr >Ba
(*d*) Ca > Sr > Ba > Mg *(A.I.P.M.T. 2015*

B24. The function of "sodium pump" is a biological process operating in each and every cell of all animals. Which of the following biologically important ions is also a constituent of this pump?
(*a*) K^+ (*b*) Fe^{2+}
(*c*) Ca^{2+} (*d*) Mg^{2+} *(A.I.P.M.T. 2015)*

B25. On heating which of the following releases CO_2 most easily?
(*a*) $MgCO_3$ (*b*) $CaCO_3$
(*c*) K_2CO_3 (*d*) Na_2CO_3 *(A.I.P.M.T. 2015)*

B26. Which of the following statement is false?
(*a*) Ca^{2+} ions are not important in maintaining the regular beating of the heart.
(*b*) Mg^{2+} ions are important in the green parts of the plants.
(*c*) Mg^{2+} ions form a complex with ATP.
(*d*) Ca^{2+} ions are important in blood clotting.
(NEET 2016)

B27. The suspension of slaked lime in water is known as
(*a*) lime water (*b*) quick lime
(*c*) milk of lime
(*d*) aqueous solution of slaked lime. *(NEET 2016)*

B28. In context with beryllium, which one of the following statement is incorrect?
(*a*) It is rendered passive by nitric acid
(*b*) It forms Be_2C
(*c*) Its salts rarely hydrolyse
(*d*) Its hydride is electron–deficient and polymeric
(NEET 2016)

B29. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field ?
(*a*) K (*b*) Rb
(*c*) Li (*d*) Na *(NEET 2017)*

B30. Which of the following oxides is most acidic in nature?
(*a*) MgO (*b*) BeO
(*c*) BaO (*d*) CaO *(NEET 2018)*

B31. Among CaH_2, BeH_2, BaH_2, the order of ionic character is
(*a*) $BeH_2 < CaH_2 < BaH_2$
(*b*) $CaH_2 < BeH_2 < BaH_2$
(*c*) $BeH_2 < BaH_2 < CaH_2$
(*d*) $BaH_2 < BeH_2 < CaH_2$ *(NEET 2018)*

Answers

B13. (*c*) **B14.** (*b*) **B15.** (*c*) **B16.** (*d*) **B17.** (*e*) **B18.** (*c*) **B19.** (*c*) **B20.** (*b*) **B21.** (*a*) **B22.** (*c*)
B23. (*c*) **B24.** (*a*) **B25.** (*a*) **B26.** (*a*) **B27.** (*c*) **B28.** (*c*) **B29.** (*c*) **B30.** (*b*) **B31.** (*a*)

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JEE Main & Other State Boards' Engineering Entrance

B32. Beryllium and aluminium exihibit many properties which are similar. But, the two elements differ in
(*a*) forming covalent halides
(*b*) forming polymeric hydrides
(*c*) exhibiting maximum covalency in compounds
(*d*) exhibiting amphoteric nature in their oxides.
(A.I.E.E.E. 2004)

B33. One mole of magnesium nitride on reaction with excess of water gives
(*a*) one mole of ammonia
(*b*) one mole of nitric acid
(*c*) two moles of ammonia
(*d*) two moles of nitric acid *(A.I.E.E.E. 2004)*

B34. Based on the lattice enthalpy and other considerations which one of the following alkali metal chlorides is expected to have highest melting point.
(*a*) LiCl (*b*) NaCl
(*c*) KCl (*d*) RbCl. *(A.I.E.E.E. 2005)*

B35. The ionic mobility of alkali metal ions in aqueous solution is maximum for
(*a*) Rb^+ (*b*) Li^+
(*c*) Na^+ (*d*) K^+ *(A.I.E.E.E. 2006)*

B36. Which of the following is formed by the action of water on Na_2O_2 ?
(*a*) H_2 (*b*) O_2
(*c*) N_2 (*d*) CO_2 *(B.H.U. 2007)*

B37. Which one of the following processes is used for the manufacture of calcium?
(*a*) Reduction of CaO with carbon
(*b*) Reduction of CaO with hydrogen
(*c*) Electrolysis of a mixture of anhydrous $CaCl_2$ and KCl
(*d*) Electrolysis of molten $Ca(OH)_2$ *(WB-JEE-2008)*

B38. RbO_2 is
(*a*) Peroxide and paramagnetic
(*b*) Peroxide and diamagnetic
(*c*) Superoxide and paramagnetic
(*d*) Superoxide and diamagnetic *(Orissa JEE 2008)*

B39. Which pair of the following chlorides do not impart colour to the flame?
(*a*) $BeCl_2$ and $SrCl_2$
(*b*) $BeCl_2$ and $MgCl_2$
(*c*) $CaCl_2$ and $BaCl_2$
(*d*) $BaCl_2$ and $SrCl_2$
(*e*) $MgCl_2$ and $CaCl_2$ *(Kerala PET 2008)*

B40. Correct order of stability of group II A metal carbonates is
(*a*) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
(*b*) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$
(*c*) $SrCO_3 > BaCO_3 > CaCO_3 > MgCO_3$
(*d*) $CaCO_3 > MgCO_3 > BaCO_3 > SrCO_3$
(Orissa JEE 2009)

B41. Which of the following oxides is most acidic in nature ?
(*a*) BeO (*b*) MgO
(*c*) CaO (*d*) BaO *(A.M.U. Engg. 2009)*

B42. Formula of gypsum is
(*a*) $CaSO_4.2H_2O$ (*b*) $CaSO_4.\frac{1}{2}H_2O$
(*c*) $3CaSO_4.H_2O$ (*d*) $2CaSO_4.2H_2O$
(Orissa JEE 2010)

B43. Which of the following metals has the largest abundance in the earth's crust ?
(*a*) Aluminium (*b*) Calcium
(*c*) Magnesium (*d*) Sodium
(West Bengal JEE 2010)

B44. The metal that produces red-violet colour in the non-luminous flame is
(*a*) Ba (*b*) Ag (*c*) Rb (*d*) Pb
(*e*) Zn *(Kerala PET 2010)*

B45. The correct order of reducing character of alkali metals is
(*a*) Rb < K < Na < Li (*b*) Li < Na < K < Rb
(*c*) Na < K < Rb < Li (*d*) Rb < Na < K < Li
(J.K. CET 2011)

B46. Among the following, the compound that is readily soluble in water is
(*a*) $BeSO_4$ (*b*) $CaSO_4$
(*c*) $SrSO_4$ (*d*) $BaSO_4$ *(J.K. CET 2011)*

B47. Which of the following represents the composition of Carnallite mineral ?
(*a*) $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$
(*b*) KNO_3
(*c*) $K_2SO_4{\cdot}MgSO_4{\cdot}MgCl_2{\cdot}6H_2O$
(*d*) $KCl{\cdot}MgCl_2{\cdot}6H_2O$ *(West Bengal JEE 2011)*

B48. Which one of the following on hydrolysis, gives the corresponding metallic hydroxide, H_2O_2 and O_2 ?
(*a*) Li_2O (*b*) Na_2O_2
(*c*) NaO_2 (*d*) Na_2O
(*e*) BeO *(Kerala PET 2011)*

B49. Be and Al exhibit diagonal relationship. Which of the following statements about them is/are not true ?
(*i*) Both react with HCl to liberate H_2.
(*ii*) They are made passive by HNO_3.
(*iii*) Their carbides give acetylene on treatment with water.
(*iv*) Their oxides are amphoteric.
(*a*) (*iii*) and (*iv*) (*b*) (*i*) and (*iii*)
(*c*) (*i*) only (*d*) (*ii*) and (*iii*)
(*e*) (*iii*) only *(Kerala PET 2011)*

Answers

B32. (*c*) **B33.** (*c*) **B34.** (*b*) **B35.** (*a*) **B36.** (*b*) **B37.** (*c*) **B38.** (*c*) **B39.** (*b*) **B40.** (*b*) **B41.** (*a*)
B42. (*a*) **B43.** (*a*) **B44.** (*c*) **B45.** (*c*) **B46.** (*a*) **B47.** (*d*) **B48.** (*c*) **B49.** (*e*)

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B50. Which one of the following order presents the correct sequence of the increasing basic nature of the given oxides ?
(a) $Al_2O_3 < MgO < Na_2O < K_2O$
(b) $MgO < K_2O < Al_2O_3 < Na_2O$
(c) $Na_2O < K_2O < MgO < Al_2O_3$
(d) $K_2O < Na_2O < Al_2O_3 < MgO$ *(AIEEE 2011)*

B51. The product obtained on heating $LiNO_3$ will be
(a) $Li_2O + NO_2 + O_2$ (b) $Li_3N + O_2$
(c) $Li_2O + NO + O_2$ (d) $LiNO_2 + O_2$ *(AIEEE 2011)*

B52. The strongest base among the following is
(a) NaOH (b) KOH
(c) LiOH (d) CsOH *(A.M.U. Engg 2012)*

B53. Among the following compounds, the one that gets hydrolysed to form metallic hydroxide, hydrogen peroxide and oxygen is
(a) Na_2O (b) Na_2O_2 (c) Li_2O (d) Li_2O_2
(e) KO_2 *(Kerala P.E.T. 2012)*

B54. The alkaline earth metal with the least density value is
(a) Mg (b) Be
(c) Sr (d) Ca
(e) Ba *(Kerala P.E.T. 2012)*

B55. The reaction between sodium and water can be made less vigorous by
(a) lowering the temperature
(b) adding a little alcohol
(c) amalgamating sodium
(d) adding a little acetic acid
(Karnataka C.E.T. 2012)

B56. Alkali metals have negative reduction potential and hence they behave as
(a) oxidising agents (b) Lewis bases
(c) reducing agents (d) electrolytes
(Karnataka C.E.T. 2013)

B57. Which of the following statement is false regarding alkali metals?
(a) Alkali metals are soft and can be cut with the help of a knife.
(b) Alkali metals donot occur is free state in nature.
(c) Alkali metals are highly electropositive elements.
(d) Alkali metal hydrides are covalent in character.
(J.K. CET 2013)

B58. The salt of alkali metal gives violet colour in the flame test. Its aqueous solution gives a white precipitate with barium chloride in hydrochloric acid medium. The salt is
(a) K_2SO_4 (b) KCl
(c) Na_2SO_4 (d) K_2CO_3
(e) Li_2SO_4 *(Kerala PET 2014)*

B59. What is the product of reaction between calcium carbide and water?
(a) Ethylene (b) Acetylene
(c) Methane (d) Benzene *(J.K. CET 2014)*

B60. The correct statement for the molecule CsI_3 is
(a) It contains Cs^+, I^- and lattice I_2 molecule
(b) It is a covalent molecule.
(c) It contains Cs^+ and I_3^- ions
(d) It contains Cs^{3+} and I^- ions. *(JEE Main 2014)*

B61. The decreasing order of basic character of K_2O, BaO, CaO and MgO is
(a) $K_2O > BaO > CaO > MgO$
(b) $K_2O > CaO > BaO > MgO$
(c) $MgO > BaO > CaO > K_2O$
(d) $MgO > CaO > BaO > K_2O$ *(WB JEE 2015)*

B62. Match the flame colours of the alkaline earth metal salts in the Bunsen burner.

(p) Calcium	1. Brick red
(q) Strontium	2. Apple green
(r) Barium	3. crimson

(a) p–1, q–3, r–2 (b) p–3, q–1, r–2
(c) p–2, q–3, r–1 (d) p–1, q–2, r–3
(WB JEE 2015)

B63. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy?
(a) $BaSO_4$ (b) $SrSO_4$
(c) $CaSO_4$ (d) $BeSO_4$ *(WB JEE 2015)*

B64. Which of the following arrangement is correct in respect of solubility in water?
(a) $CaSO_4 > BaSO_4 > BeSO_4 > MgSO_4 > SrSO_4$
(b) $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$
(c) $BaSO_4 > SrSO_4 > CaSO_4 > MgSO_4 > BeSO_4$
(d) $BeSO_4 > CaSO_4 > MgSO_4 > SrSO_4 > BaSO_4$
(WB JEE 2016)

B65. Which halide of magnesium has highest ionic character?
(a) Chloride (b) Bromide
(c) Iodide (d) Fluoride *(MH CET 2016)*

B66. The low solubility of LiF and that of CsCl in water are respectively due to which of the properties of the alkali metal ions?
(a) Higher hydration enthalpy of Li^+, higher lattice enthalpy of Cs^+
(b) Smaller hydration enthalpy of Li^+, higher lattice enthalpy of Cs^+
(c) Smaller lattice enthalpy of Li^-, higher hydration enthalpy of Cs^+
(d) Smaller hydration enthalpy of Li^+, smaller lattice enthalpy of Cs^+
(e) Higher lattice enthalpy of Li^+, smaller hydration enthalpy of Cs^+. *(Kerala PET 2016)*

Answers

B50. (a) **B51.** (a) **B52.** (d) **B53.** (e) **B54.** (d) **B55.** (c) **B56.** (c) **B57.** (d) **B58.** (a) **B59.** (b)
B60. (c) **B61.** (a) **B62.** (a) **B63.** (d) **B64.** (b) **B65.** (d) **B66.** (e)

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B67. The second ionization enthalpy of which of the following alkaline earth metals is the highest?
(a) Ba (b) Mg
(c) Ca (d) Sr
(e) Be *(Kerala PET 2016)*

B68. The main oxides formed on combustion of Li, Na and K in excess of air are, respectively
(a) Li_2O, Na_2O and KO_2
(b) LiO_2, Na_2O_2 and K_2O
(c) Li_2O_2, Na_2O_2 and KO_2
(d) Li_2O, Na_2O_2 and KO_2 *(JEE Main 2016)*

B69. Plaster of Paris is represented as
(a) $CaSO_4.2H_2O$ (b) $CaSO_4.H_2O$
(c) $CaSO_4.\frac{1}{2}H_2O$ (d) $CaSO_4$
(Karnataka CET 2017)

B70. Which of the following is covalent?
(a) NaCl (b) KCl
(c) $BeCl_2$ (d) $MgCl_2$
(e) $CaCl_2$ *(Kerala PET 2017)*

B71. One mole of an unknown compound was treated with excess water and resulted in the evolution of two moles of a readily combustible gas. The resulting solution was treated with CO_2 and resulted in the formation of white turbidity. The unknown compound is
(a) Ca (b) CaH_2
(c) $Ca(OH)_2$ (d) $Ca(NO_3)_2$
(e) $CaSO_4$ *(Kerala PET 2017)*

B72. Both lithium and magnesium display several similar properties due to the diagonal relationship; however, the one which is incorrect is :
(a) Both form basic carbonates
(b) Both form soluble biocarbonates
(c) Both form nitrides
(d) Nitrates of both Li and Mg yield NO_2 and O_2 on heating *(JEE Main 2017)*

B73. Dead burnt plaster is
(a) $CaSO_4$. (b) $CaSO_4.\frac{1}{2}H_2O$
(c) $CaSO_4.H_2O$ (d) $CaSO_4.2H_2O$
(Karnataka C.E.T. 2018)

B74. Portland cement does not contain
(a) $CaSiO_4$ (b) $CaSiO_3$
(c) $Ca_3Al_2O_6$ (d) $Ca_3(PO_4)_2$
(e) Both (c) and (d) *(Kerala P.E.T. 2018)*

B75. Which of the following is least thermally stable ?
(a) $MgCO_3$ (b) $CaCO_3$
(c) $SrCO_3$ (d) $BeCO_3$
(W.B. J.E.E. 2018)

B76. A metal on combustion in excess air forms X. X upon hydrolysis with water yields H_2O_2 and O_2 alongwith other product. The metal is
(a) Rb (b) Li
(c) Mg (d) Na *(JEE Main 2019)*

B77. The correct statement(s) among I to III with respect to potassium ions that are abundant within the cell fluids is/are :
I. They activate many enzymes
II. They participate in the oxidation of glucose to produce ATP.
III. Alongwith sodium ions, they are responsible for the transmission of nerve signals.
(a) I, II and III (b) I and III only
(c) III only (d) I and II only
(JEE Main 2019)

B78. The amphoteric hydroxide is
(a) $Ca(OH)_2$ (b) $Be(OH)_2$
(c) $Sr(OH)_2$ (d) $Mg(OH)_2$
(JEE Main 2019)

JEE (Advance) for IIT Entrance

B79. Which of the folowing process is used in the extraction of metallurgy of magnesium ?
(a) fused salt electrolysis
(b) salt reduction
(c) aqueous solution electrolysis
(d) thermite reduction. *(I.I.T. 2002)*

B80. Ammoniacal solution of $MgSO_4$ in presence of NH_4Cl is heated with Na_2HPO_4, a white precipitate is formed of
(a) $Mg(NH_4)PO_4$ (b) $Mg_3(PO_3)_2$
(c) $MgSO_4.MgCl_2$ (d) $MgSO_4.MgPO_4$ *(I.I.T. 2006)*

Answers

B67. (e) **B68.** (d) **B69.** (c) **B70.** (c) **B71.** (b) **B72.** (a) **B73.** (a) **B74.** (d) **B75.** (d) **B76.** (a)
B77. (a) **B78.** (b) **B79.** (a) **B80.** (a)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Highly pure dilute solution of sodium in liquid ammonia
(a) shows blue colour
(b) exhibits electrical conductivity
(c) forms sodium amide
(d) produces H_2 gas

C2. Which of the following is not correct order of the property mentioned?
(a) Thermal stability: $MgCO_3 < CaCO_3 < BaCO_3$
(b) Reactivity with O_2: Be < Mg < Ca
(c) Solubility in water : $MgSO_4 < CaSO_4 < SrSO_4$
(d) Enthalpy of formation : CaO < SrO < BeO

Answers

C1. (a, b) **C2.** (c, d)

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C3. Which of the following donot impart colour to the flame?
(a) Be (b) Mg (c) Ca (d) Ba

C4. Calcium oxide can be used for drying of
(a) H_2 (b) NH_3
(c) CO_2 (d) Cl_2

C5. Which of the following statements are correct?
(a) Sodium is most abundant among alkali metals.
(b) Among group I elements, radium is the only radioactive element.
(c) Lattice energy of NaI is more than that of NaBr
(d) The mobility of Li^+ in water is less than Na^+.

C6. Which of the following statements are incorrect?
(a) CaH_2 is also called hydrolith
(b) $BeCl_2$ in vapour phase exists as polymeric
(c) $MgSO_4$ is less soluble than $CaSO_4$ is water
(d) $MgCO_3$ decomposes at lower temperature than $BaCO_3$.

C7. Which of the following compounds are readily soluble in water ?
(a) $BeSO_4$ (b) $MgSO_4$
(c) $SrSO_4$ (d) $BaSO_4$

C8. Which of the following statements is/are correct.
(a) Beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
(b) Beryllium sulphate is readily soluble in water as the greater hydration enthalpy of Be^{2+} overcomes the lattice enthalpy factor.
(c) Beryllium exhibits coordination number more than four.
(d) Beryllium oxide is purely acidic in nature.

C9. The alkali metals are characterised by which of the following properties ?
(a) High boiling point
(b) High density
(c) High negative standard electrode potential
(d) Large atomic size

C10. Which of the following compounds of sodium are used for textile industry ?
(a) Na_2CO_3 (b) $NaHCO_3$
(c) NaOH (d) NaCl

C11. The compound (s) formed upon combustion of sodium metal in excess of air is (are)
(a) Na_2O_2 (b) Na_2O
(c) NaO_2 (d) NaOH *(I.I.T. JEE 2009)*

Answers

C3. (a, b) **C4.** (a, b) **C5.** (a, d) **C6.** (b, c) **C7.** (a, b) **C8.** (a, b) **C9.** (c, d) **C10.** (a, c) **C11.**(a, b)

Assertion Reason Type Questions

The questions given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer.
(a) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(b) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
(c) If assertion is CORRECT but reason is INCORRECT.
(d) If assertion is INCORRECT but reason is CORRECT.
(e) If both assertion and reason are INCORRECT.

1. Assertion : LiCl is predominantly covalent compound.
Reason : The electronegativity difference between Li and Cl is too small.

2. Assertion : Na_2SO_4 is soluble in water while $BaSO_4$ is insoluble.
Reason : Lattice energy of barium sulphate exceeds its hydration energy.

3. Assertion : $Al(OH)_3$ is amphoteric in nature.
Reason : Al–O and O–H bonds can be broken with equal lease in $Al(OH)_3$.

4. Assertion : Barium is not required for normal biological function in human.
Reason : Barium does not show variable oxidation state. *(A.I.I.M.S. 2003)*

5. Assertion : Li resembles Mg.
Reason : Li^+ has same size as Mg^{2+}.

6. Assertion : Alkali metals impart colour to the flame.
Reason : Their ionization energies are low.

7. Assertion : Sulphur is estimated as $BaSO_4$ and not as $MgSO_4$.
Reason : The ionic radius of Mg^{2+} is smaller than that of Ba^{2+}.

8. Assertion : $BeCl_2$ is covalent whereas $MgCl_2$ and $CaCl_2$ are ionic.
Reason : Beryllium is the first member of the group.

9. Assertion : Beryllium can form BeF_4^{2-} while aluminium can also form AlF_6^{3-} ion.
Reason : Beryllium does not have vacant *d*–orbitals in its outermost shell.

Answers

1. (c) **2.** (a) **3.** (a) **4.** (b) **5.** (a) **6.** (a) **7.** (b) **8.** (b) **9.** (a)

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10. **Assertion** : K, Rb and Cs can also form superoxides.
Reason : Their ionic radii increase in the order $Cs^+ < Rb^+ < K^+$.

11. **Assertion** : Cu_2Cl_2 is more covalent than NaCl.
Reason : Cu^+ ion is more polarizing than Na^+ ion.

12. **Assertion** : Be gives characteristic flame colouration.
Reason : Ionization energy of Be is high.

13. **Assertion** : Beryllium carbonate is kept in the atmosphere of carbon dioxide.
Reason : Beryllium carbonate is unstable and decomposes to give beryllium oxide and carbon dioxide.

14. **Assertion** : The carbonate of lithium decomposes easily on heating to form lithium oxide and CO_2.
Reason : Lithium being very small in size polarises large carbonate ion resulting the formation of more stable Li_2O and CO_2.

Answers

10. (c) **11.** (a) **12.** (d) **13.** (a) **14.** (a)

Matrix Match Type Questions

1. Match the element in Column I with the properties mentioned in Column II

Column I	Column II
(A) Sodium	(p) belong to third period
(B) Magnesium	(q) form insoluble sulphate
(C) Barium	(r) give characteristic flame colours
(D) Lithium	(s) form stable nitride

2. Match the compounds given in Column I with their uses given in Column II.

Column I	Column II
(A) $CaCO_3$	(p) Dentistry, ornamental work
(B) $Ca(OH)_2$	(q) Manufacture of sodium carbonate from caustic soda
(C) CaO	(r) Manufacture of high quality paper
(D) $CaSO_4$	(s) Used in white washing

Answers

1. **(A)** – (p), (r) ; **(B)** – (p), (s) ; **(C)** – (q), (r) ; **(D)** – (s)

2. **(A)** – (r) ; **(B)** – (s) ; **(C)** – (q) ; **(D)** – (p).

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. The alkali metals are low melting. Which of the following alkali metal is expected to melt if the room temperature rises to 30°C ?
(a) Na (b) K
(c) Rb (d) Cs

2. Alkali metals react with water vigorously to form hydroxides and dihydrogen. Which of the following alkali metal reacts with water least vigorously ?
(a) Li (b) Na
(c) K (d) Cs

3. The reducing power of a metal depends on various factors. Suggest the factor which makes Li, the strongest reducing agent in aqueous solution.
(a) Sublimation enthalpy
(b) Ionisation enthalpy
(c) Hydration enthalpy
(d) Electron-gain enthalpy

4. Metal carbonates decompose on heating to give metal oxide and carbon dioxide. Which of the metal carbonates is most stable thermally ?
(a) $MgCO_3$ (b) $CaCO_3$
(c) $SrCO_3$ (d) $BaCO_3$

Answers

1. (d) **2.** (a) **3.** (c) **4.** (d)

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5. Which of the carbonates given below is unstable in air and is kept in CO_2 atmosphere to avoid decomposition.
(a) $BeCO_3$ (b) $MgCO_3$
(c) $CaCO_3$ (d) $BaCO_3$

6. Metals form basic hydroxides. Which of the following metal hydroxide is the least basic ?
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Sr(OH)_2$ (d) $Ba(OH)_2$

7. Some of the Group 2 metal halides are covalent and soluble in organic solvents. Among the following metal halides, the one which is soluble in ethanol is
(a) $BeCl_2$ (b) $MgCl_2$
(c) $CaCl_2$ (d) $SrCl_2$

8. The order of decreasing ionisation enthalpy in alkali metals is
(a) Na > Li > K > Rb (b) Rb < Na < K < Li
(c) Li > Na > K > Rb (d) Li < Na < K < Rb

9. The solubility of metal halides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Amongst fluorides of alkali metals, the lowest solubility of LiF in water is due to
(a) Ionic nature of lithium fluoride
(b) High lattice enthalpy
(c) High hydration enthalpy for lithium ion
(d) Low ionisation enthalpy of lithium atom

10. Amphoteric hydroxides react with both alkalies and acids. Which of the following Group 2 metal hydroxides is soluble in sodium hydroxide ?
(a) $Be(OH)_2$ (b) $Mg(OH)_2$
(c) $Ca(OH)_2$ (d) $Ba(OH)_2$

11. In the synthesis of sodium carbonate, the recovery of ammonia is done by treating NH_4Cl with $Ca(OH)_2$. The by-product obtained in this process is
(a) $CaCl_2$ (b) NaCl
(c) NaOH (d) $NaHCO_3$

12. When sodium is dissolved in liquid ammonia, a solution of deep blue colour is obtained. The colour of the solution is due to
(a) ammoniated electron
(b) sodium ion
(c) sodium amide
(d) ammoniated sodium ion

13. By adding gypsum to cement
(a) setting time of cement becomes less.
(b) setting time of cement increases.
(c) colour of cement becomes light.
(d) shining surface is obtained.

14. Dead burnt plaster is
(a) $CaSO_4$ (b) $CaSO_4 \cdot \frac{1}{2} H_2O$
(c) $CaSO_4 \cdot H_2O$ (d) $CaSO_4 \cdot 2H_2O$

15. Suspension of slaked lime in water is known as
(a) lime water
(b) quick lime
(c) milk of lime
(d) aqueous solution of slaked lime

16. Which of the following elements does not form hydride by direct heating with dihydrogen ?
(a) Be (b) Mg
(c) Sr (d) Ba

17. The formula of soda ash is
(a) $Na_2CO_3.10H_2O$ (b) $Na_2CO_3.2H_2O$
(c) $Na_2CO_3.H_2O$ (d) Na_2CO_3

18. A substance which gives brick red flame and breaks down on heating to give oxygen and a brown gas is
(a) Magnesium nitrate (b) Calcium nitrate
(c) Barium nitrate (d) Strontium nitrate

19. Which of the following statements is true about $Ca(OH)_2$?
(a) It is used in the preparation of bleaching powder.
(b) It is a light blue solid.
(c) It does not possess disinfectant property.
(d) It is used in the manufacture of cement.

20. A chemical A is used for the preparation of washing soda to recover ammonia. When CO_2 is bubbled through an aqueous solution of A, the solution turns milky. It is used in white washing due to disinfectant nature. What is the chemical formula of A ?
(a) $Ca(HCO_3)_2$ (b) CaO
(c) $Ca(OH)_2$ (d) $CaCO_3$

21. Dehydration of hydrates of halides of calcium, barium and strontium *i.e.*, $CaCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 2H_2O$, can be achieved by heating. These become wet on keeping in air. Which of the following statements is correct about these halides ?
(a) Act as dehydrating agent
(b) Can absorb moisture from air
(c) Tendency to form hydrate decreases from calcium to barium
(d) All of the above

Multiple Choice Questions (Type-II)

22. Metallic elements are described by their standard electrode potential, fusion enthalpy, atomic size, etc. The alkali metals are characterised by which of the following properties ?
(a) High boiling point
(b) High negative standard electrode potential
(c) High density
(d) Large atomic size

Answers

5. (a) **6.** (a) **7.** (a) **8.** (c) **9.** (b) **10.** (a) **11.** (a) **12.** (a) **13.** (b) **14.** (a)
15. (c) **16.** (a) **17.** (d) **18.** (b) **19.** (a) **20.** (c) **21.** (d) **22.** (b, d)

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23. Several sodium compounds find use in industries. Which of the following compounds are used for textile industry ?
(a) Na_2CO_3 (b) $NaHCO_3$
(c) NaOH (d) NaCl

24. Which of the following compounds are readily soluble in water ?
(a) $BeSO_4$ (b) $MgSO_4$
(c) $BaSO_4$ (d) $SrSO_4$

25. When Zeolite, which is hydrated sodium aluminium silicate is treated with hard water, the sodium ions are exchanged with which of the following ion(s)?
(a) H^+ ions (b) Mg^{2+} ions
(c) Ca^{2+} ions (d) SO_4^{2-} ions

26. Identify the correct formula of halides of alkaline earth metals from the following.
(a) $BaCl_2.2H_2O$ (b) $BaCl_2.4H_2O$
(c) $CaCl_2.6H_2O$ (d) $SrCl_2.4H_2O$

27. Choose the correct statements from the following.
(a) Beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
(b) Beryllium sulphate is readily soluble in water as the greater hydration enthalpy of Be^{2+} overcomes the lattice enthalpy factor.
(c) Beryllium exhibits coordination number more than four.
(d) Beryllium oxide is purely acidic in nature.

28. Which of the following are the correct reasons for anomalous behaviour of lithium ?
(a) Exceptionally small size if its atom.
(b) Its high polarisig power.
(c) It has high degree of hydration.
(d) Exceptionally low ionisation enthalpy.

Matching Type Questions

29. Match the elements given in Column I with the properties mentioned in Column II.

Column I	*Column II*
(i) Li	(a) Insoluble sulphate
(ii) Na	(b) Strongest monoacidic base
(iii) Ca	(c) Most negative E° value among alkali metals
(iv) Ba	(d) Insoluble oxalate
	(e) $6s^2$ outer electronic configuration

30. Match the compounds given in Column I with their uses mentioned in Column II.

Column I	*Column II*
(i) $CaCO_3$	(a) Dentistry, ornamental work
(ii) $Ca(OH)_2$	(b) Manufacture of sodium carbonate from caustic soda
(iii) CaO	(c) Manufacture of high quality paper
(iv) $CaSO_4$	(d) Used in white washing

31. Match the element given in Column I with the colour it imparts to the flame given in Column II.

Column I	*Column II*
(i) Cs	(a) Apple green
(ii) Na	(b) Violet
(iii) K	(c) Brick red
(iv) Ca	(d) Yellow
(v) Sr	(e) Crimson red
(vi) Ba	(f) Blue

Assertion and Reason Type Questions

32. Assertion (A) : The carbonate of lithium decomposes easily on heating to form lithium oxide and CO_2.
Reason (R) : Lithium being very small in size polarises large carbonate ion leading to the formation of more stable Li_2O and CO_2.

33. Assertion (A) : Beryllium carbonate is kept in the atmosphere of carbon dioxide.
Reason (R) : Beryllium carbonate is unstable and decomposes to give beryllium oxide and carbon dioxide.

Answers

23. (a, c) **24.** (a, b) **25.** (b, c) **26.** (a, c) **27.** (a, c) **28.** (a, b, c)
29. (i) – (c); (ii) – (b); (iii) – (d); (iv) – (a, e) **30.** (i) – (c); (ii) – (d); (iii) – (b); (iv) – (a)
31. (i) – (f); (ii) – (d); (iii) – (b); (iv) – (c), (v) – (e); (vi) – (a) **32.** (a) **33.** (a)

Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A10. (d) : It forms paramagnetic solution.

A13. (a) : Be does not give flame colouration because of very high ionization enthalpy.

A14. (a) : Because effective (hydrated) size of Mg^{2+} ion is large.

A19. (c) : $Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$

A25. (c) : $CaSO_4.2H_2O \xrightarrow{393\ K} CaSO_4.\frac{1}{2}H_2O + \frac{3}{2}H_2O$

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B. *mcq from competitive examinations*

B1. (*b*) : In aqueous solution, because of hydration the order of effective size is :
$Na^+ > K^+ > Rb^+ > Cs^+$
Greater is size lesser is mobility.

B3. (*b*) : Basic character increases down the group.

B4. (*c*) : According to Fajan rules, larger the size of anion, greater is the covalent character.
Order of size of anions : $I^- > Br^- > Cl^- > F^-$
$\therefore$ Covalent character : MI > MBr > MCl > MF

B7. (*d*) : $CaCO_3 \longrightarrow \underset{\text{Basic oxide}}{CaO} + \underset{\text{Acidic oxide}}{CO_2}$

B11. (*a*) : Density gradually decreases on moving down a group. However, K is lighter than Na.
Li < K < Na < Rb < Cs

B12. (*b*) : LiCl being covalent is soluble in pyridine.

B13. (*c*) : Br_2 reacts with NaI only to give I_2
$2NaI + Br_2 \longrightarrow 2NaBr + I_2$

B15. (*c*) : Covalent character increases and melting point decreases :
$CaF_2 > CaCl_2 > CaBr_2 > CaI_2$

B16. (*d*) : Lithium does not form solid bicarbonate, though it exists in solution.

B18. (*c*) : Only lithium forms monoxide on heating in air.

B21. (*a*) : Calcium is responsible for neuromuscular function in the body.

B22. (*c*) : $Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{Insoluble white ppt}}{BaSO_4} + 2NaCl$
Na_2SO_4 gives yellow colour in flame test.

B23. (*c*) : Solubilities of alkaline earth metal sulphates decrease down the group. This is because, on moving down the group, hydration enthalpy decreases with increase in size of the metal ion and concequently, their solubilities decrease.

B24. (*a*) : K^+ is constituent of sodium pump.

B25. (*a*) : $MgCO_3 \xrightarrow{\text{heat}} MgO + CO_2$
Thermal stability follows the order:
$K_2CO_3 > Na_2CO_3 > CaCO_3 > MgCO_3$

B26. (*a*) : Ca^{2+} ions are important and perform important biological functions such as maintaining the regular beating of a heart.

B28. (*c*) : Beryllium salts rarely hydrolyse due to absence of *d*-orbitals.

B29. (*c*) : Li^+ is the smallest among these and has maximum electron density. Therefore, it will be heavily hydrated and its effective size in aqueous solution will be maximum among all alkali metal ions. Thus, its ionic mobility will be lowest.

B30. (*b*) : Basic character of oxides of group II increases down the group. Hence, BeO is most acidic oxide.

B31. (*a*) : Smaller the size of cation, more will be its polarising power and larger will be its covalent character. Hence, BeH_2 is least ionic and ionic character increases as :
$BeH_2 < CaH_2 < BaH_2$

B32. (*c*) : Be can have maximum covalency of 4 while Al can exhibit covalency more than 4 also.

B33. (*c*) : $Mg_3N_2 + 3H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

B40. (*b*) : On moving down the group, the size of cation increases and therefore, tendency to stability large CO_3^{2-} ion increases. Hence, stability increases.

B41. (*a*) : On moving down a group, basic character increases and acidic character decreases.

B45. (*c*) : The reduction potentials of alkali metals are :
Li(–3.04), Na(–2.72), K(–2.92), Rb(–2.93)
$\therefore$ Correct order is Na < K < Rb < Li.

B46. (*a*) : Solubility decreases down the group and therefore, $BeSO_4$ is readily soluble.

B48. (*c*) : $2NaO_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2 + O_2$

B49. (*e*) : The carbides of both Be and Al react with water and liberate methane.
$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$
$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4$

B51. (*a*) : $LiNO_3 \xrightarrow{\text{heat}} Li_2O + NO_2 + O_2$

B53. (*e*) : Superoxides (KO_2) react with water to form hydroxides, hydrogen peroxide and oxygen.
$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

B57. (*d*) : Alkali metal hydrides are ionic in character.

B58. (*a*) : Potassium and their salts give violet colour in the flame.
$K_2SO_4 + BaCl_2 \longrightarrow \underset{\text{white ppt}}{BaSO_4} + 2KCl$

B59. (*b*) : $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$

B60. (*c*) : Cs cannot show +3 oxidation state. Therefore, CsI_3 contains Cs^+ and I_3^- ions.

B61. (*a*) : Alkali metal oxides are strongly basic in nature. Down the group in alkaline earth metals, the basic character increases due to decrease in ionization enthalpy. So, the correct order of basic character is:
$K_2O > BaO > CaO > MgO$

B63. (*d*) : Be^{2+} being smaller in size has maximum hydration enthalpy which exceeds its lattice enthalpy.

B64. (*b*) : The solubility of alkaline earth metal sulphates decreases down the group because the size of metal cation increases due to which hydration enthalpies decrease.

B65. (*d*) : Smaller is the anion, less is the polarisation, more is the ionic character.

B68. (*d*) : Li forms oxide, Li_2O, Na forms peroxide, Na_2O_2 and K forms super oxide, KO_2.

B70. (*c*) : Among these $BeCl_2$ is covalent and all other are ionic compounds.

B71. (*b*) : Calcium hydride (CaH_2) on reaction with excess water evolves two moles of readily combustible H_2 gas and one mole of calcium hydroxide. The

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solution containing $Ca(OH)_2$ on treatment with CO_2 gas forms white turbidity due to the formation of $CaCO_3$.

$$CaH_2(s) + 2H_2O \longrightarrow \underset{\text{Combustible gas}}{Ca(OH)_2} + 2H_2(g)$$

$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow \underset{\substack{\text{Calcium carbonate}\\ \text{(white turbidity)}}}{CaCO_3(s)} + H_2O$$

B72. (*a*) : Mg forms basic carbonate like $3MgCO_3$. $Mg(OH)_2.3H_2O$ but Li forms only carbonate (Li_2CO_3) which is very less basic.

B73. (*a*) : Anhydrous $CaSO_4$ is known as dead burnt plaster.

B74. (*d*) : Portland cement does not contain $Ca_3(PO_4)_2$.

B75. (*d*) : For alkaline earth metals, thermal stability of metal carbonates increases down the group. Therefore, $BeCO_3$ is least thermally stable.

B76. (*a*) : $Rb + \underset{\text{excess}}{O_2} \longrightarrow RbO_2$

$$2RbO_2 + 2H_2O \longrightarrow 2RbOH + H_2O_2 + O_2$$

B78. (*b*) : $Be(OH)_2$ is amphoteric while all other are basic.

B80. (*a*) : $Mg^{2+} + NH_3 + HPO_4^{2-} \longrightarrow \underset{\text{White ppt}}{Mg(NH_4)PO_4}$

C. *mcq with more than one correct answer*

C11. (*a,b*) : $4Na + O_2 \longrightarrow 2Na_2O$

$4Na + 2O_2 \longrightarrow 2Na_2O_2$

NCERT Exemplar Problems: MCQ Type I

1. (*d*) : Melting point decreases as the strength of metallic bonding decreases with increasing size of the atom.

2. (*a*) : The reactivity of alkali metals increases down the group so that Li is least reactive.

3. (*c*) : Due to small size of Li^+ ion, its hydration enthalpy is very high.

4. (*d*) : Thermal stability of metal carbonates of alkaline earth metals increases down the group.

5. (*a*) : Due to least electropositive character or least basicity of $Be(OH)_2$, $BeCO_3$ is less stable and hence decomposes to give BeO and CO_2.

$$BeCO_3 \rightleftharpoons BeO + CO_2$$

Since the decomposition reaction is reversible, therefore, to increase the stability of $BeCO_3$ *i.e.* to reverse the equilibrium, $BeCO_3$ is kept in an atmosphere of CO_2.

6. (*a*) : Basic character of the hydroxides of alkaline earth metals increases down the group.

7. (*a*) : Due to small size and large electronegativity and high ionization enthalpy of Be, $BeCl_2$ is covalent and therefore, more soluble in organic solvents such as ethanol.

8. (*c*) : Ionisation enthalpy decreases as atomic size increases. Thus Li > Na > K > Rb.

9. (*b*) : Due to small size of Li^+ and F^- ions, the lattice enthalpy of LiF is much higher than hydration enthalpy and hence it is least soluble among alkali metal fluorides.

10. (*a*) : $Be(OH)_2$ is amphoteric and therefore, is soluble in NaOH.

11. (*a*) : $2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$. Therefore, $CaCl_2$ is the by product.

16. (*a*) : Being least reactive, Be does not form hydrides by direct heating with dihydrogen.

18. (*b*) : Calcium gives brick red colour and its nitrate breaks down to give O_2 and brown gas, NO_2.

$$2Ca(NO_3)_2 \xrightarrow{\text{heat}} 2CaO + O_2 + 4NO_2$$

NCERT Exemplar Problems: MCQ Type II

22. (*b, d*) : Alkali metals have high negative standard electrode potential and large atomic size.

24. (*a, b*) : Solubility decreases down the group because hydration enthalpy decreases but lattice enthalpies remain almost constant. Thus, $BeSO_4$ and $MgSO_4$ are soluble.

28. (*a, b, c*) : Li has exceptionally small size, high polarizing power and high degree of hydration.

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Unit Practice Test

for Board Examination

Time Allowed: 1 Hr. ***Maximum Marks: 25***

1. Name the radioactive elements of *s*-block. (1)

2. LiH is more stable than NaH. Explain. (1)

3. Name the alkali metal which floats on water without any apparent reaction with it. (1)

4. Which out of the following can be used to store an alkali metal?

C_2H_5OH, C_6H_6, H_2O (1)

5. What is the oxidation state of sodium in Na_2O_2? (1)

6. Potassium carbonate cannot be prepared by Solvay process. Why ? (2)

7. Why do beryllium and magnesium not give colour to flame whereas other alkaline earth metals do so ? (2)

8. Draw the structure of $BeCl_2$ in vapour and solid state. (2)

9. Explain the following :

(*i*) Sodium is found to be more useful than potassium.

(*ii*) Alkali metals are prepared by the electrolysis of their fused chlorides. (2)

10. Compare the stability and thermal stability of the following compounds of the alkali metals with those of alkaline earth metals :

(*i*) Carbonates

(*ii*) Nitrates

(*iii*) Sulphates (3)

11. What is diagonal relationship? Why does lithium differ from its family members but resembles magnesium? (3)

12. Explain the following :

(*a*) KO_2 is paramagnetic.

(*b*) Lithium forms oxide, sodium forms peroxide while potassium and rubidium form superoxides.

(*c*) BaO is soluble but $BaSO_4$ is insoluble in water. (3)

13. (*a*) Giving reasons arrange the following in the decreasing order of ionic mobility :

Li^+, Na^+, Rb^+, K^+

(*b*) Explain the various reactions that occur in the Solvay process for the manufacture of Na_2CO_3. (3)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part II of the book.

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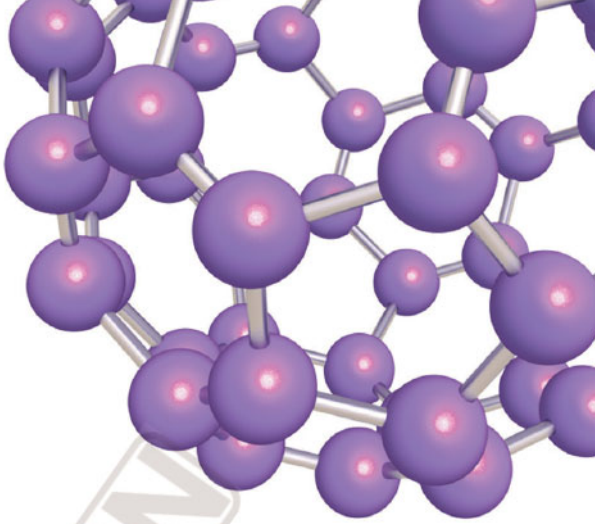
UNIT 11

SOME *p*-BLOCK ELEMENTS



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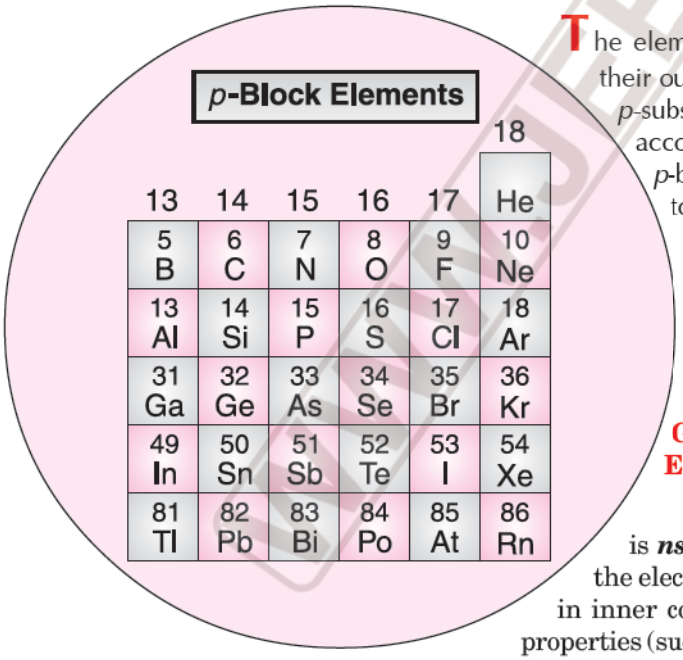
p-Block Elements
18
13 14 15 16 17 He
5 B 6 C 7 N 8 O 9 F 10 Ne
13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn

The elements in which the last electron enters the *p*-subshell of their outermost energy level are called ***p*-block elements.** Since a *p*-subshell has three degenerate *p*-orbitals, each of which can accommodate two electrons, therefore, there are six groups of *p*-block elements in the periodic table. The elements belonging to groups 13 to 18 constitute *p*-block elements. The elements boron, carbon, nitrogen, oxygen, fluorine and helium head these groups respectively. These involve the addition of one (ns^2np^1), two (ns^2np^2), three (ns^22p^3), four (ns^22p^4), five (ns^2np^5) and six (ns^2np^6) electrons respectively in *p*-orbitals, and *s*-orbitals are already filled.

GENERAL CHARACTERISTICS OF *p*-BLOCK ELEMENTS

The general electronic configuration of *p*-block elements is $\boldsymbol{ns^2np^{1-6}}$ (where n varies from 2 to 7). The inner core of the electronic configuration may however, differ. The difference in inner core of elements results in variations in their physical properties (such as atomic and ionic radii, ionisation enthalpy, electron gain enthalpy, electronegativity, etc.) as well as chemical properties. Therefore, a lot of variation in properties of a group in *p*-block elements is observed. Apart from these, in each group of the *p*-block elements, the first element differs in many respects from the other elements of the same group. Some of the significant characteristics of *p*-block elements are discussed ahead.

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Oxidation states

The oxidation states of elements are closely related to the number of electrons in the valence shell of their atoms. The maximum (or the highest) oxidation state of these elements is **numerically equal to the total number of valence electrons (*i.e.*, the sum of the *s* and *p*-electrons) or the group number minus 10.** This is also called **group oxidation state**.

Clearly, **the number of possible oxidation states increases towards the right of the periodic table.** For example, the elements of group 13 show highest oxidation state of 3 (13 –10), while those of group 14 show highest oxidation state of 4(14 – 10) and so on. In addition to group oxidation state, *p*-block elements may show other oxidation states, which normally but not necessarily differ from the total number of valence electrons by unit of two.

On descending the group, a lower oxidation state which is two units less than the highest oxidation state becomes more stable in groups 13 to 16. This trend is due to **inert pair effect.** For example, the highest oxidation state for the elements of group 13 is + 3. However, in addition to + 3 oxidation state, *these elements also show + 1 oxidation state which becomes more stable on moving down the group*. In fact, for the last element, thallium, + 1 oxidation state is more stable than + 3. Similarly, for group 14, the group oxidation state is + 4, but + 2 oxidation state becomes more and more stable on going down the group. For example, the last element, lead + 2 oxidation state is more stable than + 4 oxidation state.

This trend of occurrence of oxidation state two units less than the group oxidation state is called **inert pair effect and becomes more and more prominent as we move down the group.** This has been discussed later.

The common oxidation states displayed by the *p*-block elements are given in Table 1.

Metallic and non-metallic character

The *p*-block contains metallic and non-metallic elements. It is very interesting to note that the non-metals and metalloids exist only in the *p*-block of the periodic table.

The non-metallic character increases along a period but decreases down a group.

In fact, the heaviest element in each *p*-block group is the most metallic in nature. Therefore, the elements with most metallic character are located mostly in the lower left portion while those with most non-metallic character are present at the top right portion of the periodic table.

In between these, there are some elements which show characteristics of both metals and non-metals and are called **metalloids.** The common metalloids in *p*-block elements are B, Al, Si, Ge, As, Sb, Te, Po, At, etc. This change from non-metallic to metallic brings significant diversity in the chemistry of these elements.

In general, non-metals have higher ionization enthalpies and higher electronegativities than metals. Therefore, in contrast to metals which readily form cations, non-metals readily form anions. The compounds formed by combination of highly reactive non-metals with highly reactive metals are generally ionic in nature because of large diferences in their electronegativities. On the other hand, compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities. This can be understood in terms of their oxides.

- **Oxides of non-metals are acidic or neutral whereas**
- **Oxides of metals are basic in nature.**
- **The oxides of metalloids are amphoteric.**

Furthermore, the more electropositive the metal, the more basic is its oxide and the more electronegative the

Table 1. Common oxidation states of *p*-block elements.

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Group oxidation state	+3	+4	+5	+6	+7	+8
Various oxidation states	B +3 Al +3 Ga, In, Tl +3, +1	C +4, –4 Si +4 Ge, Sn, Pb +4, +2	N +5 to –3 P, As +3, +5, –3 Sb, Bi +3, +5	O – 1, –2 S, Se, Te –2, + 2, +4, +6	F –1 Cl, Br, I –1, +1, + 3 +5, +7	Kr + 2, +4 Xe +2, +4, +6, +8

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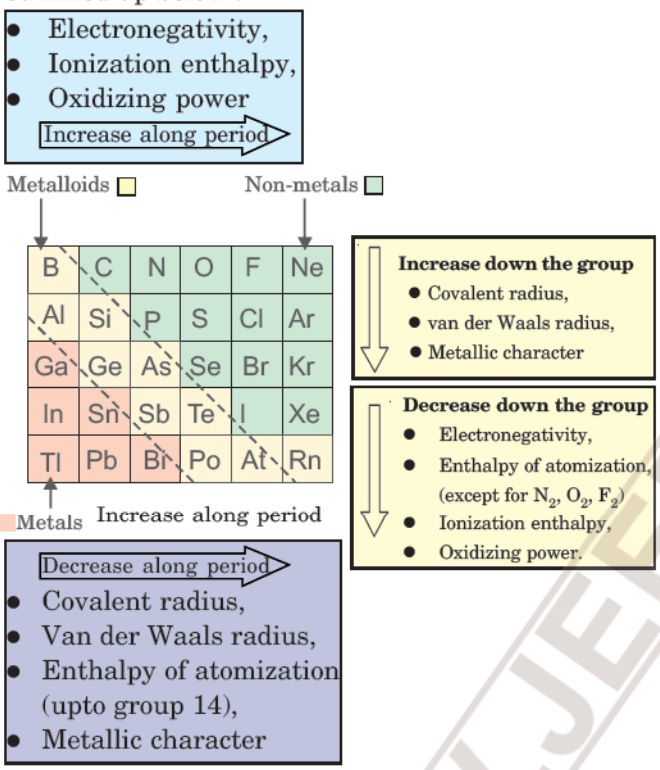
non-metal, the more acidic is its oxide. Therefore, **in *p*-block elements, acidic character of the oxides increases or basic character decreases along a period.**

Similarly, the basic character of the oxides increases or acidic character decreases down the group.

Variation in physical properties

As we shall learn in the chapter, that there is a diverse nature of elements in *p*-block. However, there are some general useful trends in their properties as summed up below :



Differences in behaviour of first element of each group

The first member of each group of *p*-block differs in many respects from its succeeding members (called **congeners**) of their respective groups. For example, boron shows anomalous behaviour as compared to rest of the members of the 13 group elements. The main reasons for the different behaviour of the first member as compared to other members is because of

(i) small size of the atom and its ion

(ii) high electronegativity and

(iii) absence of d-orbitals in their valence shell

These factors have significant effect on the chemistry of first element as compared to other elements (specially second). For example ,

(*a*) Covalence upto four. First member of each group belongs to second period elements and have only four valence orbitals *i.e.,* one 2*s* and three 2*p* orbitals available for taking part in chemical combinations. They donot have vacant *d*-orbitals in their valence shell. Therefore, they may have maximum covalence of four (using one 2*s* and three 2*p* orbitals). In contrast, the next members belonging to third or higher periods have vacant *d*-orbitals. For example, the elements of third period of *p*-block with the electronic configuration $3s^2\ 3p^x$ has vacant 3*d*-orbitals lying between 3*p* and 4*s* levels of energy. Therefore, they can easily expand their octets and can show covalence above four. For example,

(*i*) Boron forms only BF_4^- (coordination number four) whereas aluminium forms AlF_6^{3-} (coordination number six).

(*ii*) Carbon can form only tetrahalides (CX_4, X = F, Cl, Br, I) whereas other members can form hexahalides, SF_6, $SiCl_6^{2-}$ etc.

(*iii*) Nitrogen forms only NF_3 (upto octet) while phosphorus forms pentahalides, PF_5, PCl_5, etc.

(*iv*) Fluorine does not form FCl_3 (more than octet) while chlorine forms ClF_3 (extends octet).

(*b*) **Reactivity.** *Due to availability of d-orbitals of elements of third period, they are more reactive than elements of second period which do not have d-orbitals.* For example, tetrahalides of carbon are not hydrolysed by water whereas tetrahalides of other elements of group 14 are readily hydrolysed. The hydrolysis involves the nucleophilic attack of water molecule.

(*c*) **Tendency to form multiple bonds.** Because of the combined effect of smaller size and availability of *d*-orbitals, the first member of each group shows greater tendency to form $p\pi - p\pi$ multiple bonds either with itself (such as C = C, C ≡ C, N ≡ N, O = O) or with other members of the second period of elements (such as C = O, C ≡ N, N = O, etc). The other members of the group donot have strong tendency to form π- bonding. The heavier elements do form π-bonding but they involve *d*- orbitals and form $d\pi$- $p\pi$ or $d\pi$ - $d\pi$ bonding. For example, the bonds between sulphur and oxygen in oxides of sulphur (SO_2 and SO_3) are much shorter than might be expected for a single bond. In these molecules, in addition to normal σ bond, a π bond is formed by the sidewise overlap of a filled 2*p*-orbital on the oxygen with a vacant 3*d*-orbital on the sulphur (Fig. 1). This is called $p\pi$-$d\pi$ bond and results in bringing the two atoms closer and thus accounts for the shorter bond length of S—O bond.

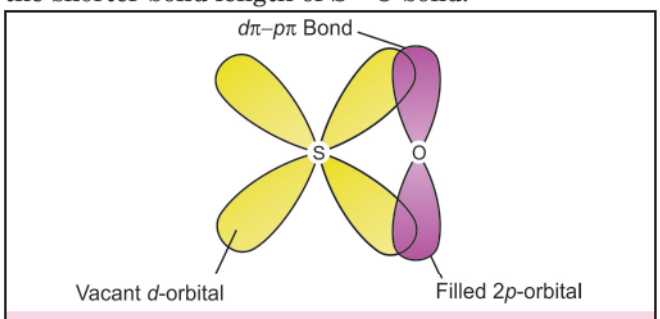


Fig. 1. Overlapping of *p* and *d* orbitals to form $p\pi$-$d\pi$ bond.

Because the *d*-orbitals are of higher energy than the *p*-orbitals, they contribute less to the overall stability of molecules than does the $p\pi$-$p\pi$ bonding of second row elements. However, the coordination number in species of heavier elements may be higher than those of first element in the same oxidation state.

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For example, both nitrogen and phosphorus form oxoanions in + 5 oxidation state as NO_3^- (three coordination with π bonding using one *p*-orbital of N) and PO_4^{3-} (having four coordination using *s*, *p* and *d* orbitals contributing to the π-bonding).

The first member of 13 group (boron) shows diagonal relationship with silicon (of group 14).

GROUP 13 ELEMENTS : BORON FAMILY

Group 13 of the periodic table consists of the elements **boron** (B), **aluminium** (Al), **gallium** (Ga), **indium** (In) and **thallium** (Tl). Except boron, which is classified as non-metal, all other elements of this group are metals. Aluminium is a metal but shows many similarities to boron (non-metal) and gallium, indium and thallium are almost exclusively metallic in character. Aluminium is the most common metallic element in the earth's crust. It is also very important element of this group because of its various industrial uses.

OCCURRENCE

Boron is fairly rare element and it occurs to a very small extent (0.0001% by mass) in earth's crust. It occurs in two allotropic forms, ^{10}B (19%) and ^{11}B (81%). It does not occur in free state but occurs as borates or orthoboric acid. The main ores of boron are :

(*i*) **Borax :**
$Na_2[B_4O_5(OH)_4].8H_2O$ or $Na_2B_4O_7.10H_2O$

(*ii*) **Kernite:**
$Na_2[B_4O_5(OH)_4]$ or $Na_2B_4O_7.2H_2O$

(*iii*) **Colemanite :**
$Ca_2[B_3O_4(OH)_3]_2.2H_2O$ or $Ca_2B_6O_{11}.5H_2O$

(*iv*) **Orthoboric acid :** H_3BO_3

The deposits of boron are found in California (U.S.A.) and in Turkey. In India, boron occurs as borax in Puga Valley of Ladakh region in Kashmir and also in Sambhar lake of Rajasthan.

Among the elements of group 13, **aluminium** is **most abundant metal.** It is **third most abundant element** (8.3% by mass) in the earth's crust after oxygen (45.5%) and silicon (25.7%). It is a major constituent of many common aluminosilicate rocks such as feldspars and micas. In India, aluminium is found as mica in Madhya Pradesh, Karnataka, Orissa, and Jammu.The important minerals of aluminium are :

(*i*) **Bauxite :** $Al_2O_3.2H_2O$. (It may also be represented as $AlO_x(OH)_{3-2x}$ where $0 < x < 1$).

(*ii*) **Cryolite** (Sodium aluminium fluoride) : Na_3AlF_6.

(*iii*) **Orthoclase** (feldspar) : $KAlSi_3O_8$

(*iv*) **Mica** (muscovite) : $KAl_2(Si_3AlO_{10})(OH)_2$

(*v*) **Beryl :** $Be_3Al_2Si_6O_{18}$

(*vi*) **Corundum** (anhydrous alumina) : Al_2O_3

Bauxite is commercially the most important ore from which aluminium metal is extracted.

Gallium, indium and thallium are very much less abundant and occur in traces in sulphide minerals rather than oxides. Small amounts of gallium are also found in the ores of elements adjacent to it in the periodic table (Al, Zn and Ge). Highest concentration (0.1-1%) of Ga is found in the rare mineral **germanite** which is a complex sulphide of Zn, Cu, Ge and As. Traces of In and Tl are found in ZnS and PbS ores. The abundance of these elements in earth's crust are given below :

Element	Abundance in earth's crust (ppm)	Relative abundance
B	9	38
Al	8.3×10^4	3
Ga	19	33
In	0.24	63
Tl	0.5	60

GENERAL CHARACTERISTICS OF GROUP 13 ELEMENTS

A. Electronic Configurations

The elements of group 13 have the general electronic configuration ns^2np^1 *i.e.,* one electron in the outermost *p*-orbitals and two electrons in the *s*-orbital. Their electronic configurations are given in Table 2.

It is clear from Table 2 that boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 *d*-electrons core while thallium has noble gas plus 14 *f*-electrons and 10 *d*-electrons core. Thus, the electronic configurations of elements of group 13 are more complex than those of groups 1 and 2. This difference in electronic configurations affects the other properties and consequently the chemistry of this group.

Table 2. Electronic configurations of the elements of group 13

Element	Symbol	Atomic Number	Electronic Configuration
Boron	B	5	[He] $2s^2\ 2p^1$
Aluminium	Al	13	[Ne] $3s^2\ 3p^1$
Gallium	Ga	31	[Ar] $3d^{10}\ 4s^2\ 4p^1$
Indium	In	49	[Kr] $4d^{10}\ 5s^2\ 5p^1$
Thallium	Tl	81	[Xe] $5d^{10}\ 6s^2\ 6p^1$

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Table 3. Physical constants of Group 13 elements.

Property	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Atomic mass	10.81	26.96	69.72	114.82	204.38
Atomic radius (pm)	85	143	135	167	170
Ionic radius (pm) M^{3+}	27	53.5	62.0	80.0	88.5
Ionic radius, M^+ (pm)	–	–	120	140	150
Density (g cm^{-3})	2.35	2.70	5.90	7.31	11.85
Ionization enthalpy (kJ mol^{-1})					
IE_1	801	577	579	558	590
IE_2	2427	1816	1979	1820	1971
IE_3	3659	2744	2962	2704	2877
Density (g cm^{-3} at 293 K)	2.35	2.70	5.90	7.31	11.85
Electronegativity	2.0	1.5	1.6	1.7	1.8
Density (g cm^{-3} at 293 K)	2.35	2.70	5.90	7.31	11.85
Melting point (K)	2453	933	303	430	576
Boiling point (K)	3923	2740	2676	2353	1730
E° (M^{3+}/M) (V)	–	– 1.66	– 0.56	– 0.34	+ 1.26
E° (M^+ / M) (V)	–	+ 0.55	– 0.79 (acid) – 1.39 (alkali)	– 0.18	– 0.34

B. Atomic and Physical Properties

The important atomic parameters and physical constants of group 13 elements are given in Table 3 and their general physical characteristics are discussed below :

1. Atomic and ionic radii

The atomic and ionic radii of group 13 elements are smaller as compared to corresponding elements of group 2.

Explanation. This is due to the increase in nuclear charge when we move from element of group 2 to group 13 in the same period. As we move from left to right in the period, the magnitude of nuclear charge increases but the electrons are added to the same shell. Since the electrons in the same shell do not screen each other, therefore, the electrons experience greater nuclear charge. In other words, effective nuclear charge increases and thus, size decreases. Therefore, the elements of this group have smaller size than the corresponding elements of second group.

On moving down the group both atomic and ionic radii are expected to increase due to the addition of new shells. However, the observed atomic radius of Al (143 pm) is slightly more than that of Ga (135 pm).

Explanation. While going from Al (Z = 13) to Ga (Z = 31) there are also ten elements of the first transition series of *d*-block from (Z = 21 to 30) which have electrons in the inner *d*-orbitals. The *d*-orbitals do not screen the nucleus effectively because of their shapes and poor penetration power. As a result, the effective nuclear charge in Ga becomes more than in Al and its atomic radius, therefore, decreases slightly.

2. Ionisation enthalpies

The first ionisation enthalpies of group 13 elements are less than the corresponding members of the alkaline earths.

Explanation. We know that the first electron in the case of group 13 elements (ns^2np^1) is to be removed from *p*-orbital while in case of elements of group 2, the electron has to be removed from *s*-orbital. Since *p*-orbitals are at slightly higher energy than the *s*-orbitals, the electron in the atoms of group 13 elements is weakly held by the nucleus and, therefore, the first ionisation enthalpy is less. However, second (IE_2) and third (IE_3) ionisation enthalpies are quite high. As expected, the order of ionisation enthalpies is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$. The sum of the first three ionisation enthalpies for each of these elements is very high. This will be affecting the chemical properties of these elements as discussed later. When one electron is removed from outermost *p*-subshell, the resulting ion has completely filled *s*-orbital (ns^2). Therefore, it becomes difficult to remove the second electron.

On moving down the group, there is a sharp decrease in first ionisation enthalpy (Δ_iH_1) from B to Al and then first ionisation enthalpy of Ga is unexpectedly slightly higher (about 2 kJ mol^{-1}) than that of Al. Then again the first ionisation enthalpy decreases from Ga to In while that of Tl is much higher than those of Al, Ga and In. Thus, amongst the elements of group 13, B has the highest and In has the lowest Δ_iH_1.

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Explanation. The sharp decrease in ionisation enthalpy from B to Al is due to increase in atomic size and screening effect which is more than to compensate the effect of increase in nuclear charge. Consequently, the electron becomes less and less tightly held by the nucleus as we move down the group. Hence, *ionisation enthalpy decreases down the group from B to Al*. In case of Ga, there are ten *d*-electrons in its inner sub shell. Since the *d*-electrons shield the nuclear charge less effectively than the *s*- and *p*-electrons, and therefore, due to poor shielding of ten *d*-electrons the outer electron is held fairly strongly by the nucleus. As a result, *the ionisation enthalpy increases slightly* inspite of the increase in atomic size as we move from Al to Ga.

Further, on moving down the group from Ga to In, although nuclear charge increases but the total shielding effect of 3*d*- and 4*d*- electrons outweighs the effect of increased nuclear charge and therefore, Δ_iH_1 *of In is lower than that of Ga*. On further moving from In to Tl, there is increase in Δ_iH_1 similar to that from B to Al. This is due to the presence of 14 *f*-electrons in inner electronic configuration of Tl which have very poor shielding effect. As a result, effective nuclear charge acting on Tl is much higher than that on In and hence Δ_iH_1 *of Tl is much higher than that of In even higher than those of Ga and Al*. Thus, *the anomalous behaviour in general decrease down the group 13 elements is due to the presence of ten d-electrons after Al and 14 f-electrons after In which have poor shielding effect.*

3. Electronegativity

The electronegativities of group 13 elements are more than those of elements of group 1(alkali metals) and group 2 (alkaline earth metals). In group 13, the electronegativity first decreases from B to Al and then increases down the group.

Explanation. As we move from B to Al, the atomic size increases considerably. Therefore, attraction of the nucleus for the electrons decreases and hence electronegativity decreases. On further moving down the group, although the size increases (except that of Ga), yet the effective nuclear charge increases because of poor shielding of the inner *d*- and *f*- electrons. As a result, the force of attraction of the nucleus for the electrons increases and hence the electronegativity increases from Al to Tl.

4. Melting and boiling points

The melting and boiling points decrease on moving down the group. However, the decrease in melting point is not as regular as in boiling points.

Boron is non-metallic in nature. It is extremely hard and black coloured solid. Boron has very strong crystalline lattice and therefore it has very high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity. Gallium has very low melting point (303 K) and therfore could exist in liquid state during summer. It melts in our hands in summer because of its low melting point. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.

Boron exists in four common allotropic forms under different conditions. The transition between different forms is extremely slow process. All these boron allotropes are built up of basic building B_{12} icosahedral units made up of polyhedron having 20 faces as shown in Fig. 2. These are *amorphous boron* (dark brown colour) and *crystalline boron* (black metallic lustre).

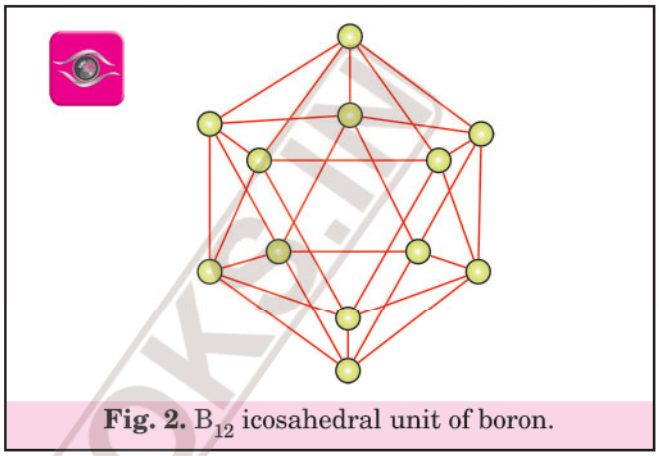

Fig. 2. B_{12} icosahedral unit of boron.

5. Electropositive (or metallic) character

Due to high ionisation enthalpies, the elements of group 13 are less electropositive as compared to elements of group 2. On moving down the group, the electropositive (metallic) character increases because ionisation enthalpy decreases. For example, boron is a non-metal while the other elements are typical metals.

C. Oxidation States

The atoms of these elements have three valence electrons, two in *s*-subshell and one in *p*-subshell. Therefore, *all these elements can show maximum of +3 oxidation state*.It may also be noted that due to the small size of boron, the sum of its first three ionisation enthalpies is very high. Therefore, it cannot form +3 ions and can only form covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases and is therefore, able to form Al^{3+} ions. In fact, aluminium is highly electropositive metal. However as we move down the group, due to poor shielding effect of intervening *d* and *f*-orbitals, the increased effective nuclear charge holds *ns* electrons very tightly (responsible for inert pair effect) restricting their participation in bonding. As a result, only *p*-orbitals may be involved in bonding. Thus, the elements of group 13 exhibits +3 and +1 oxidation states.

Boron shows only +3 oxidation state in its compounds. Except boron, the other elements also show + 1 oxidation state. The + 1 oxidation state becomes more stable as we move down the group from aluminium to thallium.

$$Al < Ga < In < Tl.$$

In fact, in Ga, In and Tl, both +3 and +1 oxidation states are observed. However, in Ga and In, +3 oxidation state is more stable than +1 oxidation state. As a result, both Ga^+ and In^+ salts disproportionate in water i.e., undergo self oxidation and reduction as:

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$$3\,\overset{+1}{Ga}\,X\,(s) \longrightarrow 2\overset{0}{Ga} + \overset{+3}{Ga^{3+}}\,(aq) + 3X^-(aq)$$

$$3\overset{+}{In}\,X\,(s) \longrightarrow 2\,\overset{0}{In} + \overset{+3}{In^{3+}}\,(aq) + 3X^-(aq)$$

In case of last element, thallium, + 1 oxidation state has been found to be more stable than + 3 oxidation state in aqueous solution. This is evident from the redox potential as :

$$Tl^{3+}\,(aq) + 2e^- \rightleftharpoons Tl^+\,(aq)\quad E^{\ominus} = +1.25\ V$$

It may be noted that gallium, the third element of the group appears to show +2 oxidation state in some of its compounds such as $GaCl_2$. However, it has been shown that this compound has the structure $Ga^+[GaCl_4]^-$ which contains gallium in +1 (Ga^+) and +3($GaCl_4^-$) oxidation states.

Explanation. This is explained on the basis of **inert pair effect.** The elements of group 13 have three electrons in their valence shell (ns^2np^1) and, therefore, exhibit, oxidation state of + 3. However, it has been observed that in addition to + 3 oxidation state, they also exhibit oxidation state of +1. The +1 oxidation state becomes more and more stable as we go down the group from B, Al, Ga, In to Tl. For example, the +1 oxidation state of Tl is more stable than +3 oxidation state. Thus, thallous compounds such as TlOH and TlCl are more stable than their corresponding thallic compounds. This is due to the fact that in the case of last element, after the removal of one electron from *p*-orbital, the remaining ns^2 (*e.g.* $6s^2$) electrons behave like stable noble gas and do not take part in compound formation. ***This reluctance of the s-electron pair to take part in chemical combination*** *is called* **inert pair effect.** As a result of inert pair effect, the heavier elements of *p*-block show oxidation states two units less than the group oxidation state. This helps to explain the stability of lower oxidation states for the heavier elements of a group.

The decreasing stability of the higher oxidation state (+3) with increasing atomic number arises because of the decrease in bond energy with size from Al to Tl. As a result, the energy required to unpair the ns^2 electrons is not compensated by the energy released in forming the two additional bonds.

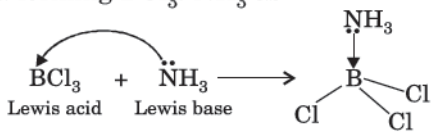
D. Chemical Properties

Except boron, the other elements of group 13 show metallic character which increases down the group. Boron is non-metallic and the crystalline form is very hard, inert and non-conducting. The amorphous form of boron is more reactive. Aluminium is also reactive metal but it usually gets covered with a protective oxide layer which makes it inert to acids, although it is attacked by alkalies. Gallium, indium and thallium are relatively soft and reactive metals which readily dissolve in acids.

The first three ionisation enthalpies of boron are quite higher than the corresponding values for the other elements of group 13. Therefore, the total energy needed to form B^{3+} ion is much greater than that compensated by lattice energies (in solids) or hydration energies (in aqueous solutions). As a result, ionic compounds of boron are not easily formed. Boron can readily form covalent compounds by sharing.

Unlike boron, the other atoms of group 13 form ionic compounds in aqueous solution. For example, the compounds of aluminium are both ionic and covalent. For example, $AlCl_3$ is covalent while $[Al(H_2O)_6]^{3+}$ is ionic.

Except thallium, all other elements form compounds in trivalent state. In trivalent state, the number of electrons around the central atom in a molecule of these elements will be only six. For example, boron forms boron halides such as BF_3, BCl_3, BBr_3, BI_3 etc. in which boron has only six electrons around it. Such compounds have two electrons less than the octet and therefore, are called **electron deficient molecules.** These have tendency to accept a pair of electrons to achieve stable electronic configuration and therefore, behave as **Lewis acids.** For example, BCl_3 readily combines with donors (Lewis bases) such as amines, ethers, etc. For example, BCl_3 readily accepts a lone pair of electrons from ammonia forming BCl_3. NH_3 as



The *Lewis acid character of these compounds decreases down the group as the size of the element increases i.e.,*

$BX_3 > AlX_3 > GaX_3 > InX_3$

where X = F, Cl, Br, I

$AlCl_3$ achieves stability by forming dimer Al_2Cl_6 (discussed later). Most of the compounds in trivalent state being covalent are readily hydrolysed by water. For example, trichlorides of boron on hydrolysis with water give tetrahedral $[M(OH)_4]^-$ species. In this case, the hybridisation of M is sp^3. On the other hand, $AlCl_3$ in acidified solution gets hydrolysed to form octahedral $[Al(H_2O)_6]^{3+}$ ion. In this complex, 3*d* orbitals of Al are also used involving $sp^3\,d^2$ hybridisation.

Let us discuss some common chemical properties of group 13 elements.

1. Reactivity towards air

Pure boron is almost unreactive at ordinary temperature. Aluminium reacts readily in air, even at ordinary temperature forming a thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form boron trioxide and aluminium oxide. With nitrogen, they form nitrides.

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$$4E(s) + 3O_2(g) \xrightarrow{\text{Heat}} 2E_2O_3(s)$$

e.g., $4B(s) + 3O_2(g) \xrightarrow{\text{Heat}} 2B_2O_3(s)$

$$4Al(s) + 3O_2(g) \xrightarrow{\text{Heat}} 2Al_2O_3(s)$$

$$2E(s) + N_2(g) \xrightarrow{\text{Heat}} 2EN(s)$$

e.g., $2B(s) + N_2(g) \xrightarrow{\text{Heat}} 2BN(s)$

$$2Al(s) + N_2(g) \xrightarrow{\text{Heat}} 2AlN(s)$$

The nature of oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in nature.

2. Reactivity towards water

Pure boron does not react with water. Aluminium is also not attacked by cold water. However, aluminium amalgamated with mercury becomes very reactive and decomposes even cold water liberating hydrogen.

$$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2$$

Gallium and indium are attacked neither by cold water nor by hot water unless oxygen is present. Thallium is a little more reactive than gallium and forms an oxide on the surface.

3. Reactivity towards acids and bases

Boron does not react with acids and alkalies even at moderate temperature. However, it is attacked at high temperatures by strong oxidising acids such as a mixture of hot conc. H_2SO_4 and HNO_3 (2 : 1) forming boric acid.

$$B(s) + 3HNO_3(aq) \xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4} \underset{\text{Boric acid}}{H_3BO_3(aq)} + 3NO_2(g)$$

Boron also reacts with fused caustic alkalies like NaOH and KOH forming corresponding borates and liberates dihydrogen.

$$2B(s) + 6NaOH(s) \xrightarrow[>773\,K]{\text{Fused}} \underset{\text{Sodium borate}}{2Na_3BO_3(s)} + 3H_2(g)$$

Boron also dissolves in fused Na_2CO_3 and $NaNO_3$ mixture at 1123 K.

$$2B(s) + 3Na_2CO_3(s) + 3NaNO_3(s) \longrightarrow \underset{\text{Sodium borate}}{2Na_3BO_3(s)} + 3NaNO_2(s) + 3CO_2(g)$$

Aluminium dissolves in mineral acids as well as aqueous alkalies and this shows its amphoteric character.

$$2Al(s) + 6HCl(aq) \longrightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$$

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow \underset{\text{Sodium tetrahydroxoaluminate (III) ion}}{2Na^+[Al(OH)_4]^-(aq)} + 3H_2(g)$$

However, *concentrated nitric acid makes aluminium passive by forming a protective layer of its oxide (Al_2O_3) on the surface.*

$$2Al(s) + 6HNO_3(conc.) \longrightarrow Al_2O_3 + 6NO_2 + 3H_2O$$

This protects it from further action.

Gallium, indium and thallium dissolve in dilute acids liberating hydrogen. Gallium is amphoteric like aluminium and it dissolves in aqueous NaOH liberating H_2 and forming gallates.

$$2Ga(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow \underset{\text{Sodium tetrahydroxogallate (III)}}{2Na^+[Ga(OH)_4]^-(aq)} + 3H_2(g)$$

In and Tl, however, donot react with alkalies.

4. Reactivity towards halogens

These elements react with halogens to form trihalides.

$$2E(s) + 3X_2 \longrightarrow 2EX_3(g)$$

E = Element of 13 Group, X = F, Cl, Br and I

e.g., $2B + 3X_2 \longrightarrow 2BX_3$ (X = F, Cl, Br, I)

IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Let us discuss some of the chemical reactivity trends of elements of group 13.

1. Formation of hydrides

The group 13 elements form hydrides of the general formula EH_3. The thermal stability of these hydrides decreases as we go down the group.

Boron forms a number of hydrides having the general formula B_nH_{n+4} and B_nH_{n+6}. These compounds of boron and hydrogen are called **boranes.** For example, B_2H_6, B_4H_{10}, B_5H_{11} etc. These contain special types of bonds known as *multicentre bonds*. The simplest among the boranes is **diborane** (B_2H_6).

Aluminium forms polymeric hydrides of the general formula $(AlH_3)_n$. Other members form less stable hydrides.

These hydrides are weak Lewis acids and readily form adducts with strong Lewis bases (:B) of the type EH_3 : B (where E = Al or Ga). Therefore, they form complex hydrides like lithium aluminium hydride $Li[AlH_4]$, lithium boron hydride $Li[BH_4]$ and lithium gallium hydride $Li[GaH_4]$. The formation of these hydrides is due to the presence of vacant *p*-orbital in their outermost shells which readily takes electron pair from hydride ion (H^-), and form tetra hydrido anions such as $[EH_4]^-$

$$XH_3 + H^- \longrightarrow [XH_4]^-$$

where X = B, Al, Ga.

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The complex hydrides act as **powerful reducing agents.** $Li[AlH_4]$ is also prepared by the action of LiH with $AlCl_3$ in ether as :

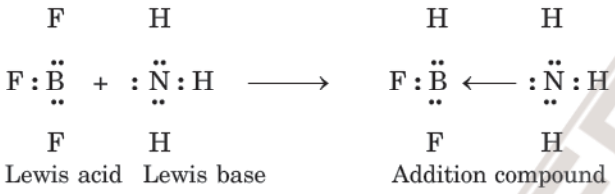
$$4LiH + AlCl_3 \xrightarrow{\text{Ether}} Li[AlH_4] + 3LiCl$$

It is a white crystalline solid and soluble in diethyl ether. It is very powerful reducing agent.

2. Formation of halides

All the elements of group 13 form **trihalides** of the general formula EX_3 (except TlI_3). The halides of boron are **covalent** and **monomeric** in vapour phase. In these halides, boron involves sp^2 hybridisation using one (2*s*) and two (2*p*) orbitals. The sp^2 hybrid orbitals adopt **trigonal planar structure.** Each of the sp^2 hybrid orbital overlaps with the 2*p*-orbital of halogen to form B—X bonds. A 2*p*-orbital is left vacant in the valence shell (Fig. 3).

All the halides of boron are volatile, highly reactive and monomeric. BF_3 and BCl_3 are gases at room temperature. BBr_3 is a volatile liquid while BI_3 is a solid. In these compounds, the octet of boron is not complete because they have only six electrons around boron. Therefore, these halides act as **Lewis acids** and combine with donors (Lewis bases) such as amines, ethers, sulphides or phosphines. For example,



The **relative Lewis acid strength of boron halides increases as :**

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

This order is just **reverse** of what may be expected on the basis of the electronegativities of the halogen atoms. Since F is most electronegative among the halogens, it will withdraw electrons from boron atom strongly. As a result, it will make BF_3 as the most electron deficient and strongest Lewis acid. However, BF_3 is the least acidic among the trihalides of B. This **anomalous** behaviour can be explained on the basis of the tendency of the halogen atom to back donate its electrons to the boron atom. This is explained below :

As already discussed, there is one 2*p*-vacant orbital on B atom in BF_3 and 2*p*-orbital of each F atom is fully filled. Since the energies of these two 2*p*-orbitals (of B and F) are almost similar, one of the 2*p* filled orbital of F overlaps sidewise with the vacant 2*p*-orbital of B atom resulting in the transference of electrons from F atom to vacant 2*p* orbitals. Thus, B—F bond acquires some double bond (or $p\pi$—$p\pi$ bond) character. The type of bond is called **dative** or **back bonding.**

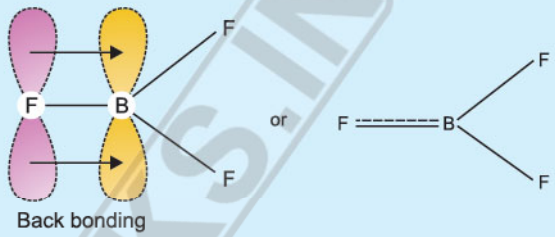


Fig. 4. Formation of $p\pi$—$p\pi$ back bonding in one of the B—F bonds in BF_3.

The back bonding in BF_3 molecule also gets support from the fact that the observed B—F bond length in BF_3 (1.30 Å) is significantly shorter than the sum of the covalent radii (B = 0.80 Å and F = 0.72 Å) or normal B—F single bond.

As a result of the **back donation** *of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and, therefore, the Lewis acid character of BF_3 decreases.* The tendency to form $p\pi$—$p\pi$ bond is maximum in the case of BF_3 and decreases rapidly as we move to BCl_3 to BBr_3 and BI_3. This is because of the inability of the vacant 2*p*-orbital of boron to overlap effectively with the 3*p*- orbital of chlorine in B—Cl bond and the 4*p*-orbital of bromine in B—Br bond and the *sp*-orbital of iodine in B—I bond due to the appreciable differences in their energy levels.

Halides of other elements of Group III also behave as Lewis acids. The **Lewis acid strength decreases as :**

$$B > Al > Ga > In.$$

In contrast to boron halides, aluminium halides exist as **dimeric molecules.** The halides of Al in the vapour state as well as in inert organic solvents such as benzene exist as dimers. For example, $AlCl_3$ exists

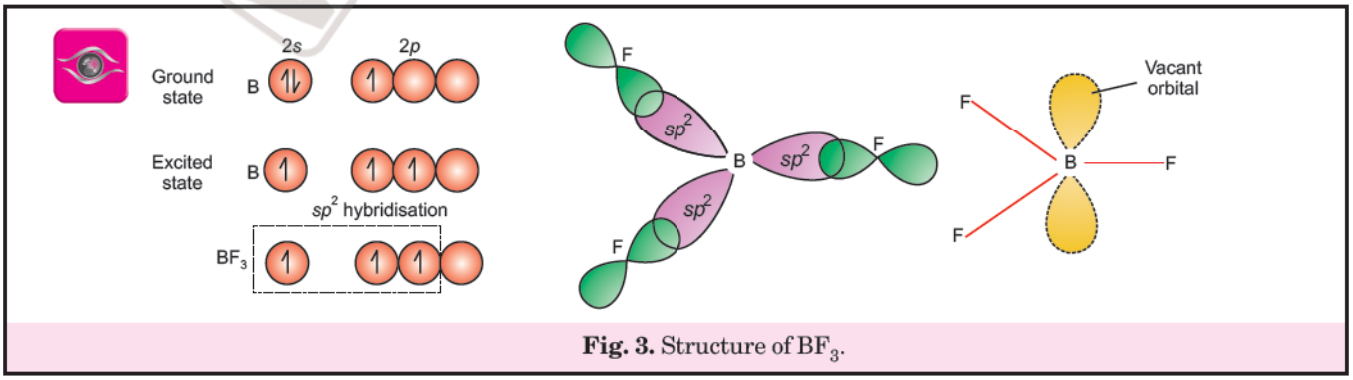


Fig. 3. Structure of BF_3.

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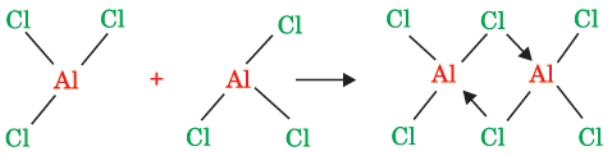
as Al_2Cl_6. The formation of dimer is illustrated below :



Two $AlCl_3$ molecules Dimer

In $AlCl_3$, there are six electrons around Al atom and these are two less than the octet. In the dimeric structure, each aluminium atom completes its octet by accepting a lone pair of electrons from the chlorine atom of another aluminium chloride molecule. The two co-ordinate covalent Cl—Al bonds are shown in the figure, in which the arrow indicates the donation of electrons from chlorine to aluminium.

The dimer structure exists only in vapour state and at low temperature (473 K) but at higher temperature, it dissociates to trigonal planar $AlCl_3$ molecule.

It may be noted *that anhydrous* **$AlCl_3$ is covalent** *in nature but* **hydrated aluminium chloride** is **ionic.** In anhydrous $AlCl_3$, Al atom is linked to three Cl atoms by covalent bonds. This is due to the fact that a large amount of energy is needed to convert aluminium atom to aluminium ion (Al^{3+}). Therefore, it prefers to form covalent bonds with Cl atoms. However, when aluminium chloride is dissolved in water, it undergoes hydration as :

$$Al_2Cl_6 + nH_2O \rightleftharpoons 2\,[Al(H_2O)_6]^{3+} + 6Cl^- + \text{Energy}$$

Hydration of Al_2Cl_6 is an exothermic process and a large amount of hydration energy is released. Thus, energy liberated during hydration process is responsible for the removal of three electrons from Al and forms Al^{3+} ion. In fact, in dissolved state, Al exists as $[Al(H_2O)_6]^{3+}$. Therefore, the hydrated aluminium chloride is ionic in nature.

The trihalides of all other elements of group 13 except Tl(III) iodide are known. The fluorides are generally ionic and have high melting points. The chlorides, bromides and iodides all have low melting points and are mainly covalent.

Characteristic structural difference between trihalides of B and Al

There is a **characteristic difference** in the structures of trihalides of boron and aluminium. For example, $AlCl_3$ exists as **dimer** Al_2Cl_6 while BCl_3 exists as **monomer.** It is interesting to note that both B and Al are electron deficient compounds and behave as Lewis acids but aluminium chloride exists as dimer whereas boron chloride exists as monomer. *This is due to the reason that boron atom is very small in size and it cannot accommodate four large sized halide ions around it to form dimer.*

3. Oxides and hydroxides

All the elements of group 13 form oxides of general formula E_2O_3 and hydroxides $E(OH)_3$. The oxides of B and Al are obtained by heating the metal in oxygen.

$$4B + 3O_2 \longrightarrow 2B_2O_3$$
$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

The hydroxides are generally obtained by dissolving the oxides of the element in water. However, boron oxide does not react with water even in the form of steam. The basic character of oxides and hydroxides decreases from aluminium to thallium. The oxides and hydroxides of B are **weakly acidic** and therefore, react with alkalies :

$$B_2O_3 + 2NaOH \longrightarrow \underset{\text{Sod. metaborate}}{2NaBO_2} + H_2O$$
$$B(OH)_3 + NaOH \longrightarrow \underset{\text{Sod. metaborate}}{NaBO_2} + 2H_2O$$

Aluminium oxide and hydroxide are **amphoteric** in nature. They dissolve both in acids as well as in alkalies.

$$Al_2O_3(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$$
$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

Similarly,

$$Al(OH)_3(s) + NaOH(aq) \longrightarrow \underset{\substack{\text{Sodium tetrahydroxoaluminate (III)}\\ \text{or } NaAlO_2.2H_2O\\ \text{Sodium aluminate}}}{Na[Al(OH)_4](aq)}$$
$$Al(OH)_3(aq) + 3HCl(aq) \longrightarrow AlCl_3(aq) + 3H_2O(l).$$

Like $Al(OH)_3$, $Ga(OH)_3$ is also *amphoteric.* Indium hydroxide, $In(OH)_3$ and thalous hydroxide TlOH are basic. $Tl(OH)_3$ is insoluble in water while Tl(OH) is soluble and is a strong base. Many of Tl(*I*) compounds are similar to corresponding alkali metal compounds.

Therefore, the **basic character of oxides and hydroxides increases** as

B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	Tl_2O_3
$B(OH)_3$	$Al(OH)_3$	$Ga(OH)_3$	$In(OH)_3$	TlOH
Acidic	Amphoteric		Basic	

Basic character increases

Explanation. As we move down the group, the magnitude of the ionisation energy decreases. As a result, the strength of the M–O bond also decreases accordingly. Therefore, its cleavage becomes easy resulting in the increased basic strength down the group. The acidic strength of the hydroxides, therefore, decreases.

4. Behaviour of Compounds

Except for boron, the trichlorides, bromides and iodides of all these elements are hydrolysed by water. These exist as $[M(OH)_4]^-$ tetrahedral and $[M(H_2O)_6]^{3+}$ octahedral species in aqueous medium.

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Aluminium sulphate forms double salts with sulphates of other metals such as E $Al(SO_4)_2.12H_2O$ where E is a univalent cation, Na^+ or K^+. These are called **alums**. These alums are used in the softening of hard water and as mordant in dyeing and printing of textiles. The mordant helps to bind the dye to the fabric.

The (+1) oxidation state becomes more and more stable from Ga to Tl. For example, the mono halides, GaX, InX, TlX are known (X = Cl, Br and I). But GaX and InX disproportionate in water as :

$3\ EX(s) \longrightarrow 2E(s) + E^{3+}(aq) + 3X^-(aq)$

However, Tl(I) is stable.

USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

Uses of Boron

Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity finds many applications. Some important applications of boron are :

(*i*) It is used as a semi-conductor for making electronic devices.

(*ii*) It is used in steel industry for increasing hardness of steel. Boron has infact replaced expensive metals like Mo, Cr and W in the manufacture of special hard steels.

(*iii*) Its compounds such as borax and boric acid are used in glass industry for making heat resistant glass i.e., pyrex glass, glass-wool and fibre glass.

(*iv*) Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as a constituent of medical soaps. An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

(*v*) Boron fibres are used in making bullet proof vests and light composite materials for aircrafts.

(*vi*) Metal borides are used in atomic reactors as protective shields and central rods because of the high tendency of B-10 ($^{10}_{5}B$) isotope to neutrons. This special property of B-10 isotope absorb neutrons is also of latest interest in the possible use of boron compounds in *Cancer Chemotherapy*.

(*vii*) Boron compounds are finding use as rocket fuels because of their high energy/mass ratio.

(*viii*) Boron is an essential element in plant metabolism.

Uses of Aluminium

Aluminium is a bright silvery white metal, with very high tensille strength. It has high electrical and thermal conductivity. Some important applications of aluminium are :

(*i*) Aluminium metal is light, soft, non-toxic and corrosion resistant. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper. Therefore, it is extensively used in household utensils, in chemical plants and as structural metal for aircrafts, ships, cars, heat exchangers, etc.

(*ii*) It is also used for making electric power cables.

(*iii*) Aluminium foil is used for packing chocolates, cigarettes, food items, etc.

(*iv*) Aluminium is also used for making cans for drinks, beer, dairy products and containers for chemicals and tooth paste tubes.

(*v*) Alumina is used in making refractory bricks and ultra marines and alums are used in dyeing and paints.

(*vi*) Many of the mechanical properties of pure Al are greatly improved by alloying it with Cu, Mn, Sn, Ni, Mg, Zn, etc. These alloys can be given shapes of pipes, tubes, rods, wires, plates or foils and therefore, have many uses in different fields. Some of the alloys of aluminium are given in Table 4.

It may be noted that the use of aluminium and its compounds for domestic purposes is now discouraged because of their toxic nature.

The other metals Ga, In and Tl have no large scale uses. Small amounts of Ga are used to dope crystals for making transistors. It find uses in solid state devices as GaAs. It is also used in low melting solder and other low melting alloys. Thallium as a metal does not find worthwhile uses, though its salts find a number of uses. Its compounds are used in preparing optical glasses because of their high refractive indices. TlBr and TlI have been used in spectroscopy and as infrared detectors, and as photosensitive diodes. Thallium carboxylates have been used in organic synthesis.

Table 4: Important alloy of aluminium

Alloy	Composition	Properties	Uses
Aluminium bronze	Al 95% Cu 5%	Light, strong alloy with golden lustre, resistant to corrosion	For making coins, utensils, picture frames, jewellary etc.
Magnalium	Al 95% Mg 5%	Very light, tough and hard	For making light instruments, balance beams, pressure cookers, etc
Duralumin	Al 95% Cu 4% Mg 0.5% Mn 0.5%	Light, strong, ductile, resistant to water, corrosion	For making bodies of aircrafts, helicopters, automobile parts kitchenware, bodies of ships, etc.
Alnico	Al, Ni, Co, Fe	Highly magnetic in nature	For making powerful magnets.

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ANOMALOUS PROPERTIES OF BORON

Boron, the first member of group 13, shows anomalous behaviour and differs from rest of the members of its family. This may be due to

(*i*) exceptionally small atomic size and ionic size

(*ii*) its high ionisation enthalpy.

(*iii*) absence of d-orbitals in its valence shell.

Some important properties in which boron differs from the rest of the members of its group (especially the next member, Al) are given below:

(*i*) Boron being small is harder than other elements of its group.

(*ii*) It has higher melting and boiling points than other members of its group.

(*iii*) Boron forms only covalent compounds whereas all other members of its group form ionic as well as covalent compounds. For example, BF_3 is covalent while Al F_3 is ionic.

(*iv*) The oxide and hydroxide of boron are weakly acidic and dissolve in alkalies forming metaborates. The oxides and hydroxides of Al and Ga are amphoteric while those of In and Tl are basic.

$$B_2O_3 + 2NaOH \longrightarrow 2NaBO_2 + H_2O$$
$$B(OH)_3 + NaOH \longrightarrow NaBO_2 + 2H_2O$$

The oxides of Al are amphotesic and react with alkalies and acids.

$$Al_2O_3 + 2\,NaOH \longrightarrow 2NaAlO_2 + 2H_2O$$
$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

(*v*) The trihalides of group 13 being covalent are hydrolysed by water. The boron trihalides form only tetrahedral species $[B(OH)_4]^-$ because of the absence of *d*-orbitals. But the trihalides of Al and other elements, due to the presence of *d*-orbitals form octahedral $[Al\,(H_2O)_6]^{3+}$ species.

(*vi*) The trihalides of boron are monomeric. This is because of its small size, it cannot accommodate four large sized halogen atoms around it. The monomeric trihalides being electron deficient, behave as strong Lewis acids and therefore, form complexes with ammonia, alcohols, ethers, etc.

$$H_3N: + BF_3 \longrightarrow H_3N \longrightarrow BF_3$$

On the other hand, the trihalides of Al and other elements of the group form bridged dimeric structures in which the metal completes its octet by accepting an electron pair from a halogen atom of the other molecule.

SOME IMPORTANT COMPOUNDS OF BORON

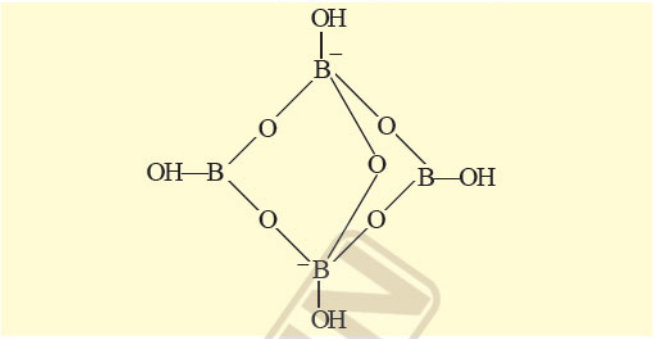
Some useful compounds of boron are discussed below:

1. Borax, $Na_2[B_4O_5(OH)_4].\,8H_2O$ or $Na_2B_4O_7.10H_2O$

Borax or sodium tetraborate is an important compound of boron. It occurs naturally *as tincal* (*suhaga*) in certain dried up lakes of India, Tibet, Ceylon and California.

Borax contains the tetranuclear units $B_4O_5(OH)_4]^{2-}$ and therefore, its correct formula is $Na_2[B_4O_5(OH)_4].\,8H_2O$.

The structure of $[B_4O_5(OH)_4]^{2-}$ ion is given below:



Preparation of Borax

1. From tincal. Borax is obtained from tincal by boiling it with water. The solution is filtered to remove insoluble impurities of sand, clay, etc. The solution is concentrated till the crystals of borax separate out.

2. From colemanite. Borax can also be prepared from the mineral colemanite ($Ca_2B_6O_{11}$) by boiling with sodium carbonate solution to form borax and sodium metaborate.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow{\text{Heat}} 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

(ppt) Borax Sodium metaborate

The precipitate of calcium carbonate is filtered off and the solution upon concentration and cooling gives crystals of borax. Sodium metaborate present in the mother liquor can be converted to borax by passing carbon dioxide through it.

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

Sodium metaborate — Sodium tetraborate

3. From boric acid. Borax can also be prepared in small quantities from boric acid by neutralizing it with sodium carbonate.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

On cooling crystals of $Na_2B_4O_7.10H_2O$ separate out.

Properties of Borax

(*i*) It is a white crystalline solid.

(*ii*) Borax dissolves in water to give alkaline solutions due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

Orthoboric acid (weak acid) (strong alkali)

(*iii*) On heating, borax decomposes and swells losing water of crystallisation. On further heating, it melts into a transparent liquid which solidifies to a transparent glass like bead which consists of boric anhydride (B_2O_3) and sodium metaborate ($NaBO_2$).

$$Na_2B_4O_7.\,10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 + 10H_2O$$
$$Na_2B_4O_7 \xrightarrow{\text{Heat}} 2NaBO_2 + B_2O_3$$

Sod. metaborate — Boric anhydride (Transparent glassy bead)

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When the glassy bead is touched with some coloured cations such as Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, etc. and heated again, it gives characteristic coloured beads of metaborates of different ions. The test is performed on a platinum wire with the salts containing these cations. Upon heating, the salts are converted into their oxides which form coloured metaborates with boron oxide. This is known as **borax bead test.**

$$NiO + B_2O_3 \longrightarrow Ni(BO_2)_2$$
Nickel metaborate (brown)

$$CoO + B_2O_3 \longrightarrow Co(BO_2)_2$$
Cobalt metaborate (blue)

$$Cr_2O_3 + 3B_2O_3 \longrightarrow 2Cr(BO_2)_3$$
Chromium metaborate (green)

$$MnO + B_2O_3 \longrightarrow Mn(BO_2)_2$$
Manganese oxide — Manganese metaborate (pink)

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$$
Cupric oxide — Cupric metaborate (blue)

Certain metaborates are reduced to the free metal in a reducing flame by the carbon. For example,

$$2Cu(BO_2)_2 + C \longrightarrow 2CuBO_2 + B_2O_3 + CO$$
Cupric metaborate (Blue) — Cuprous metaborate (colourless)

$$2CuBO_2 + C \longrightarrow 2Cu + B_2O_3 + CO$$
Metal (red)

(*iv*) On adding calculated amount of sodium hydroxide to borax, sodium metaborate is formed.

$$Na_2B_4O_7 + 2NaOH \longrightarrow 4NaBO_2 + H_2O$$
Sodium metaborate

(*v*) On adding calculated amount of hot concentrated sulphuric acid to a hot concentrated solution of borax, boric acid is formed.

$$Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$$
$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3$$
Boric acid

Uses of Borax

(*i*) Borax is used in the laboratory for borax bead test.
(*ii*) It is used in the manufacture of enamels and glazes for earthen pots.
(*iii*) It is used in the candle industry
(*iv*) It is used in the preparation of medicinal soaps due to its antiseptic character.
(*v*) It is used in making optical glass.
(*vi*) It is used in softening of water and cleansing agent.

2. Orthoboric acid, H_3BO_3 or $B(OH)_3$

Boric acid is trivial name for *orthoboric acid.*

Preparation of Boric acid

1. From borax. It is usually prepared by acidifying an aqueous solution of borax. The resulting solution upon concentration and cooling gives crystals of boric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$
$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$$

2. From colemanite. The powdered mineral colemanite is boiled with water. Sulphur dioxide is passed through the solution when boric acid and calcium bisulphite are formed.

$$Ca_2B_6O_{11} + 11H_2O \longrightarrow 2Ca(OH)_2 + 6H_3BO_3$$
$$2Ca(OH)_2 + 4SO_2 \longrightarrow 2Ca(HSO_3)_2$$

$$Ca_2B_6O_{11} + 11H_2O + 4SO_2 \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

Calcium bisulphite is highly soluble in water while boric acid is very sparingly soluble which separates out on cooling.

3. From hydrolysis of boron compounds. It can also be prepared by the hydrolysis of boron compounds (*e.g.* halides, hydrides, etc.)

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$
$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

Properties of Boric acid

(*i*) It is a white crystalline solid with a soft soapy touch.
(*ii*) It is sparingly soluble in cold water but fairly soluble in hot water.
(*iii*) On heating, orthoboric acid loses molecules of water in stages at different temperatures and forms different products.
(*a*) At 373 K, it forms metaboric acid by losing a water molecule.

$$H_3BO_3 \xrightarrow{373\ K} HBO_2 + H_2O$$
Metaboric acid

(*b*) When metaboric acid is heated at 433 K, tetraboric acid is formed.

$$4HBO_2 \xrightarrow{433K} H_2B_4O_7 + H_2O$$
Tetraboric acid

On further heating to red hot, it swells up giving a frothy mass and finally forms boron trioxide.

$$H_2B_4O_7 \xrightarrow{\text{Red hot}} 2B_2O_3 + H_2O$$
Boron trioxide

The complete **action of heat** on boric acid may be written as :

$$H_3BO_3 \xrightarrow{373\ K} HBO_2 \xrightarrow{433\ K} H_2B_4O_7 \xrightarrow{\text{Red hot}} B_2O_3$$
Boric acid — Metaboric acid — Tetraboric acid — Boron oxide

(*iv*) **Acidic character.** Boric acid is a weak monobasic acid ($K_a = 1.0 \times 10^{-9}$). It may be noted that boric acid does not act as a *protonic acid* (*i.e.* proton donor) but behaves as a ***Lewis acid*** by accepting a pair of electrons from OH^- ion.

$$H\text{—}OH + B(OH)_3 \longrightarrow [B(OH)_4]^- + H^+$$
$$B(OH)_3 + 2H\text{—}O\text{—}H \longrightarrow [B(OH)_4]^- + H_3O^+$$

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(*v*) **Action with ethyl alcohol.** With ethyl alcohol, in the presence of H_2SO_4, boric acid reacts to form ethyl borates.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{Ethyl borate}}{B(OC_2H_5)_3} + 3H_2O$$

The vapours of ethyl borate *burn in air with green flame.* This is the basis for detecting borates and boric acid in qualitative analysis.

Uses of Boric acid

(*i*) Boric acid is used in the manufacture of enamels and pottery glazes.
(*ii*) It is used as a food preservative in food industry.
(*iii*) It is used in the manufacture of pigments and borax.
(*iv*) It is used in medicines as an eye wash.

Structure of Boric acid

Boric acid has the unit BO_3^{3-} ions. These have trigonal planar structure. Boron atom in ground state has the outer electronic configuration as $2s^2 2p^1$. In the excited state, one of the electrons from 2*s*-orbital is promoted to 2*p*-orbital making three unpaired electrons. The boron atom undergoes sp^2 hybridisation and each sp^2 hybrid orbital overlaps with 2*p*-orbital of O^- forming three B—O^- bonds.Therefore, BO_3^{3-} has trigonal planar structure as shown in Fig. 5.

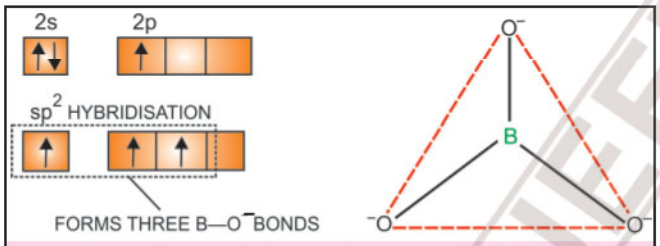

Fig. 5. Trigonal planar structure of BO_3^{3-} ion.

Orthoboric acid has a layer structure in which BO_3^{3-} units are linked through hydrogen bonds forming a *larger structure* as shown in Fig. 6. It is clear from the figure that each B-atom is bonded to three oxygen atoms and each oxygen atom is bonded to a hydrogen atom.

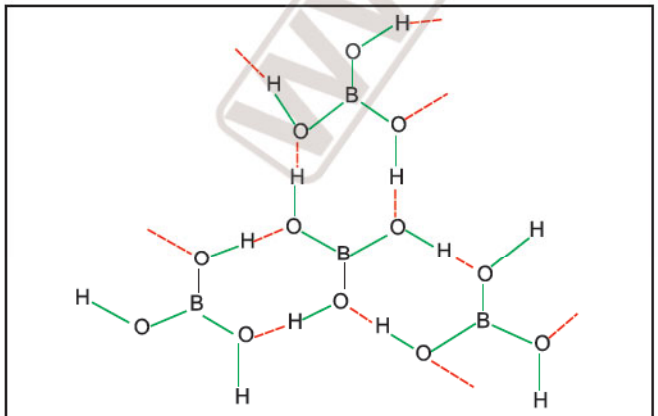

Fig. 6. Structure of orthoboric acid (dotted lines represent hydrogen bonds.

3. Boron Hydrides

Boron forms a number of hydrides having the general formula B_nH_{n+4} and B_nH_{n+6}. These compounds of boron and hydrogen are called **boranes.** For example,

(*i*) **B_nH_{n+4} boranes:** B_2H_6 (diborane), B_5H_9 (pentaborane –9), B_6H_{10} (hexaborane–10), $B_{10}H_{14}$ (decaborane-14) etc.
(*ii*) **B_nH_{n+6} boranes:** B_4H_{10} (tetraborane), B_5H_{11} (pentaborane–11), B_6H_{12} (hexaborane–12), B_8H_{14} (octaborane –14), etc.

These contain special types of bonds known as *multicentre bonds*. The simplest among the boranes is **diborane** (B_2H_6), as discussed below :

Preparation of diborane. In the laboratory, diborane is prepared by the reaction of iodine on sodium borohydride in a high boiling solvent such as polyether. In this case sodium borohydride is oxidised with iodine.

$$2NaBH_4 + I_2 \xrightarrow{\text{Polyether}} B_2H_6 + 2NaI + H_2$$

It can also be prepared by the treatment of boron trifluoride or boron trichloride with $LiAlH_4$ in diethyl ether.

$$4BF_3 + 3LiAlH_4 \xrightarrow{\text{Diethyl ether}} 2B_2H_6 + 3LiF + 3AlF_3$$

$$4BCl_3 + 3LiAlH_4 \xrightarrow{\text{Diethyl ether}} 2B_2H_6 + 3AlCl_3 + 3LiCl$$

On an industrial scale, diborane is prepared by the reaction of BF_3 with lithium hydride or sodium hydride at 450 K.

$$2BF_3 + 6LiH \xrightarrow{450\ K} B_2H_6 + 6LiF$$

$$2\ BF_3 + 6\ NaH \xrightarrow{450\ K} B_2H_6 + 6NaF$$

The higher boranes are formed when diborane (B_2H_6) is heated at 373–523 K.

Properties of diborane

(*i*) Diborane is a colourless, highly toxic gas with boiling point of 180 K and melting point of 108 K.

(*ii*) It catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$
$$\Delta_c H^\circ = -1976\ kJ\ mol^{-1}$$

It has higher heat of combustion per unit mass than other substances except hydrogen. Therefore, it is used as a high energy fuel.

(*iii*) Diborane is stable only at low temperatures. When heated at temperatures between 373 K and 523 K, it changes to a number of higher boranes.

$$B_2H_6 \xrightarrow{\text{Heat}} B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, \text{etc.}$$

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The careful control of temperature, pressure and reaction time enables the yield of different boranes. For example, B_4H_{10} is best prepared by storing B_2H_6 under pressure at 298 K for 10 days.

$$2B_2H_6 \xrightarrow[200\ atm,\ 5\ hr]{353-363\ K} B_4H_{10} + H_2$$
(15% yield)

(*iv*) Boranes are readily hydrolysed by water liberating H_2 gas.

$$B_2H_6 + 6H_2O \longrightarrow \underset{\text{Boric acid}}{2H_3BO_3} + 6H_2$$

(*v*) With alkali metal hydrides in diethyl ether, boranes form complex borohydrides.

$$2LiH + B_2H_6 \longrightarrow \underset{\text{Lithium borohydride}}{2Li[BH_4]}$$

(*vi*) Diborane reacts with ammonia and give different products depending upon the conditions. Initially, it gives B_2H_6. $2NH_3$ formulated as $[BH_2(NH_3)_2]^+ BH_4^-$. This gives boron or borazine on heating. When treated with excess of NH_3 at high temperature, diborane gives boron nitride $(BN)_x$.

$$3B_2H_6 + 6NH_3 \longrightarrow \underset{\text{Diammoniate of diborane}}{3[BH_2(NH_3)_2]^+ BH_4^-}$$

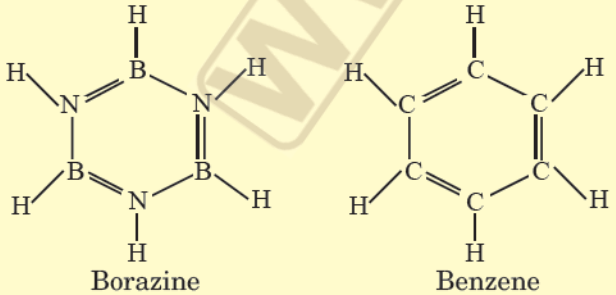
$$\downarrow \text{Heat, 450 K}$$

$$\underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$$

or $$3B_2H_6 + 6NH_3 \xrightarrow{450\ K} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$$

$$B_2H_6 \xrightarrow[\text{High temp.}]{\text{Excess } NH_3} \underset{\text{Boron nitride}}{(BN)_x}$$

Borazine has structure similar to benzene and therefore, it is called **inorganic benzene.** In this structure, both B and N atoms are sp^2 hybridised. Each N atom has one lone pair of electrons while each B atom has empty *p*-orbital. The π-bonding of borazine is dative and it arises because of sidewise overlapping of fully filled *p*-orbitals of N and empty *p*-orbitals of B. The structure of borazine is shown below alongwith the structure of benzene.



Borazine Benzene

Because of the similarity of borazine and benzene, borazine is also known as **inorganic benzene.**

Boron nitride, $(BN)_x$ is a giant molecule and resembles graphite in its structure.

(*vii*) Diborane gives addition reactions with Lewis bases (L) to give borane adducts BH_3L.

$$B_2H_6 + 2CO \longrightarrow \underset{\text{Borine carbonyl}}{2BH_3 . CO}$$

$$B_2H_6 + 2NMe_3 \longrightarrow 2BH_3 . NMe_3$$

(*viii*) Diborane dissolves in strong alkali solutions (NaOH or KOH) giving metaborates and hydrogen is evolved.

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow \underset{\text{Potassium metaborate}}{2KBO_2} + 6H_2$$

(*ix*) Diborane reacts with halogen acids to give halodiboranes and evolving hydrogen. The order of reactivity of halogen acids is HI > HBr > HCl. HI reacts at about 323 K in the absence of catalyst while HBr and HCl react in the presence of their respective aluminium halides.

$$B_2H_6 + HI \xrightarrow{323\ K} B_2H_5I + H_2$$

$$B_2H_6 + HBr \xrightarrow{AlBr_3} B_2H_5Br + H_2$$

$$B_2H_6 + HCl \xrightarrow{AlCl_3} B_2H_5Cl + H_2$$

(*x*) Diborane reacts with halogens under different conditions to form halodiboranes.

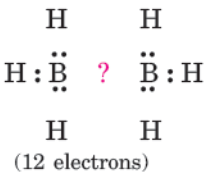
$$B_2H_6 + Cl_2 \xrightarrow[\text{Explosive}]{298\ K} \underset{\text{Chlorodiborane}}{B_2H_5Cl} + HCl$$

$$B_2H_6 + Br_2 \xrightarrow[\text{Rapid}]{373\ K} \underset{\text{Bromodiborane}}{B_2H_5Br} + HBr$$

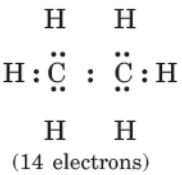
$$B_2H_6 + I_2 \longrightarrow \underset{\text{Iododiborane}}{B_2H_5I} + HI$$

Structure of diborane

The structure of diborane is very puzzling. Boron atom in the excited state has the configuration $2s^1\ 2p_x^{\ 1} 2p_y^{\ 1}$. It has only three electrons available for sharing. Now, if boron forms all conventional covalent bonds as in ethane (C_2H_6), 14 electrons are required (six B–H bonds and one B–B bond). But there are only 12 electrons (six from two boron atoms and six from hydrogen atoms). Thus, the molecule is short of two electrons.



(12 electrons)



(14 electrons)

Thus, it cannot have structure similar to ethane. The electron diffraction studies have shown bridged structure for diborane as shown in Fig. 7 ahead.

In this structure there are *two types of hydrogen atoms.* Four hydrogen atoms (2 on the left and 2 on the right) are known as **terminal hydrogens.**

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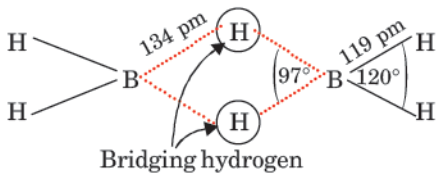
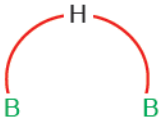


Fig. 7. Structure of diborane.

These are different than the other two hydrogen atoms, which are known as **bridged hydrogens.** The two boron atoms and the four terminal H-atoms lie in the same plane while the two bridging H-atoms are in a plane perpendicular to the rest of the molecule. There are two types of bonds in the molecule :

(*i*) The four terminal hydrogens are bonded by normal covalent bonds formed by sharing of one electron each by B and H-atoms.

(*ii*) The bridged hydrogens are different than the normal electron pair bonds. These are bonded by **three centre electron pair bonds,** which involve one electron pair only (two electrons) but binds three atoms, B, H and B. Such a bond is indicated by

H ··· B ··· H or 

and is known as **three centre electron pair bond.**

There are two such type of bonds in diborane.

This structure can be explained on the basis of hybridisation. Boron in the excited state has the electronic configuration : $2s^1 2p_x^1 2p_y^1 2p_z^0$. The boron atom undergoes sp^3 hybridisation involving 2*s* and all the three 2*p* orbitals including one empty orbital. The four sp^3 hybrid orbitals adopt tetrahedral arrangement as shown in Fig . 8. The vacant hybrid orbital is shown by dotted lines. Two hybrid orbitals of each B atom overlaps with 1*s* orbitals of two H atoms. Of the two hybrid orbitals left on each B atom, one contains an unpaired electron while the other is vacant. The hybrid orbital containing an unpaired electron of one B atom and the vacant hybrid orbital of the second B atom overlaps simultaneously with 1*s* orbital of a H atom to form B—H—B bridge bond as shown in Fig. 8(*a*). This bond involves three atoms (two B atoms and one H atom) and contains only two electrons (because one overlapping B orbital is empty). Therefore, this B—H—B bond is called **three centre electron pair bonds.** Because of the typical shape of this bond, it is also called **banana bond.** The structure of diborane is shown in Fig. 8(*b*).

Uses of diborane

(*i*) Diborane is used for preparing a number of other boron hydrides such as $LiBH_4$, $NaBH_4$, etc.

(*ii*) It is used as a reducing agent in organic reactions.

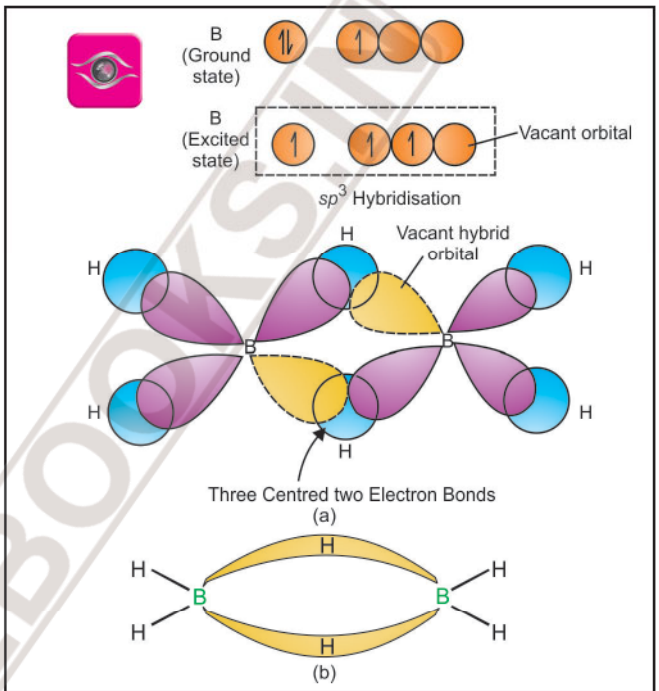


Fig 8. Structure of diborane on the basis of hybridisation.

(*iii*) It is used as a fuel for supersonic rockets.

Hydridoborates

Boron also forms a series of hydridoborates and the most important among these is the tetrahedral $[BH_4]^-$ ion. Tetrahydridoborates of several metals are known. For example, lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with diborane in diethyl ether.

$$2MH + B_2H_6 \longrightarrow 2M^+[BH_4]^- \ (M = Li \text{ or } Na)$$

Both $LiBH_4$ and $NaBH_4$ are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

These are discussed in detail in unit 9.

SOLVED EXAMPLES

❑ **Example 1.**

Write balanced equation for the reaction of elemental boron with

(i) Oxygen (ii) Nitrogen (iii) Chlorine at high temperatures.

Solution : (*i*) $4B + 3O_2 \xrightarrow{\text{Heat}} 2B_2O_3$

Boron trioxide

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(*ii*) $2B + N_2 \xrightarrow{Heat} \underset{\text{Boron nitride}}{2BN}$

(*iii*) $2B + 3Cl_2 \longrightarrow \underset{\text{Boron trichloride}}{2BCl_3}$

❑ Example 2.

Write balanced equation for the preparation of elemental boron by reduction of BBr_3 with dihydrogen.

Solution: $2BBr_3 + 3H_2 \longrightarrow 2B + 6HBr$

❑ Example 3.

Write balanced equations for :

(*i*) $BF_3 + LiH \longrightarrow$

(*ii*) $NaH + B_2H_6 \longrightarrow$

(*iii*) $H_3BO_3 \xrightarrow{Heat}$

(*iv*) $Al + NaOH \longrightarrow$

(*v*) $B_2H_6 + NH_3 \longrightarrow$

(*vi*) $BCl_3 + H_2O \longrightarrow$

(*vii*) $B_2H_6 + H_2O \longrightarrow$

Solution: (*i*) $2BF_3 + 6LiH \xrightarrow{450K} \underset{\text{Diborane}}{B_2H_6} + 6LiF$

(*ii*) $2\,NaH + B_2H_6 \longrightarrow \underset{\text{Sodium borohydride}}{2\,Na\,[BH_4]}$

(*iii*) $H_3BO_3 \xrightarrow[373\,K]{Heat} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$

$4HBO_2 \xrightarrow[-H_2O]{Heat} H_2B_4O_7 \xrightarrow{Heat} \underset{\text{Boron trioxide}}{2B_2O_3} + H_2O$

(*iv*) $2Al + 2NaOH + 6H_2O \longrightarrow 2Na[Al(OH)_4] + 3H_2$

(*v*) $B_2H_6 + 2NH_3 \longrightarrow 2BH_3.NH_3$

(*vi*) $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$

(*vii*) $B_2H_6 + 6H_2O \longrightarrow \underset{\text{Ortho boric acid}}{2H_3BO_3} + 6H_2$

❑ Example 4.

What happens when

(i) Borax is heated strongly

(ii) Boric acid is added to water

(iii) Aluminium is treated with HCl.

Solution: (*i*) On heating borax first loses water molecules and swells up. On further heating it turns to transparent liquid which solidifies into glass like material called borax bead.

$\underset{\text{Borax}}{Na_2B_4O_7.10H_2O} \xrightarrow{Heat} Na_2B_4O_7 \xrightarrow{Heat} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$

(*ii*) It acts as Lewis acid

$\underset{\text{Boric acid}}{B(OH)_3} + H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$

(*iii*) Liberates hydrogen

$2Al + 6HCl \longrightarrow 2Al^{3+} + 6Cl^- + 3H_2$

❑ Example 5.

Standard electrode potential values, E° of Al^{3+}/Al is –1.66 V and that of Tl^{3+}/Tl is 1.26 V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of two metals.

N.C.E.R.T.

Solution: Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to form Al^{3+} (*aq*) ions. Whereas thallium has lesser tendency than Al. Tl^{3+} is not only unstable but it is a powerful oxidising agent also. Thus, Tl^+ is more stable in solution than Tl^{3+}.

Aluminium being able to form +3 ion easily is more electropositive than thallium.

❑ Example 6.

White fumes appear around the bottle of aluminium chloride. Why ? **N.C.E.R.T.**

Solution: Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture and liberates HCl gas. Moist HCl appears white in colour.

$AlCl_3(s) + 3H_2O\,(l) \longrightarrow Al(OH)_3(s) + 3HCl(g)$

❑ Example 7.

A certain salt X, gives the following results :

(i) Its aqueous solution is alkaline to litmus.

(ii) It swells up to a glassy meterial Y on strong heating.

(iii) When conc. H_2SO_4 is added to a hot solution of X, white crystals of an acid Z separate out.

Write equations for all the above reactions and identify X, Y and Z. **N.C.E.R.T.**

Solution: (*i*) Since the aqueous solution of salt (X) is alkaline, it must be the salt of a strong base and a weak acid. X is borax, $Na_2B_4O_7.10H_2O$. It dissolves in water to give alkaline solution due to the formation of strong base (NaOH).

$\underset{\text{Borax (X)}}{Na_2B_4O_7.10H_2O} \xrightarrow{Water} \underset{\text{Weak acid}}{H_2B_4O_7} + \underset{\text{Strong base}}{2NaOH} + 8H_2O$

(*ii*) On heating it swells up because it loses water molecules.

On strong heating, a glassy bead is formed.

$Na_2B_4O_7.\,10H_2O \xrightarrow{Heat} Na_2B_4O_7 \xrightarrow{Heat} 2Na\underbrace{BO_2 + B_2O_3}_{\text{Glassy bead (Y)}}$

(*iii*) When conc. H_2SO_4 is added to a hot solution of X i.e., borax, white crystals of an acid (Z) separate out. The Z must be the crystals of boric acid.

$Na_2B_4O_7.\,10H_2O + H_2SO_4 \longrightarrow \underset{\text{Boric acid (Z)}}{4H_3BO_3} + Na_2SO_4 + 5H_2O$

❑ Example 8.

Boron is unable to form BF_6^{3-} ion. Explain.

N.C.E.R.T.

Solution: Boron does not have vacant *d*-orbitals in its valence shell. Therefore, it cannot expand its octet. Therefore, maximum covalency of boron cannot exceed four and it does not form BF_6^{3-} ion.

❑ Example 9.

Account for the fact that aluminium chloride exists as a dimer.

Solution: In $AlCl_3$, there are six electrons around Al and are two less than the octet. So, Al in $AlCl_3$ is *electron*

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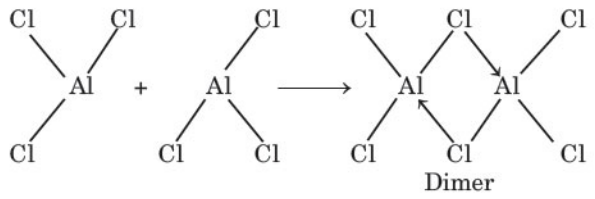
deficient whereas Cl atom has a lone pair of electrons to donate. Therefore, each Al atom completes its octet by accepting a lone pair from Cl atom of another aluminium chloride molecule. Thus, it forms a dimer.



❑ Example 10.

Why is boric acid considered as a weak acid ?

N.C.E.R.T.

Solution: Boric acid is not able to release H^+ ions of its own. It receives OH^- ions from water to complete its octet and therefore, releases H^+ ions. Therefore, it is a weak acid.

❑ Example 11.

Why does boron not form B^{3+} ions ?

Solution: Boron has very small size and has very high sum of three ionisation enthalpies ($IE_1 + IE_2 + IE_3$). Therefore, it cannot lose its three electrons to form B^{3+} ions.

❑ Example 12.

Aluminium forms $[AlF_6]^{3-}$ but boron does not form $[BF_6]^{3-}$ ion. Why ?

Solution: Boron does not have vacant *d*-orbitals in its valence shell and hence cannot extend its octet. It cannot show covalency more than four. However, Al has vacant *d*-orbitals in its valence shell and can show a covalency of six.

❑ Example 13.

A compound (A) of boron reacts with NMe_3 to give an adduct (B) which on hydrolysis gives a compound (C) and hydrogen gas. Compound (C) is an acid. Identify the compounds A, B and C. Give the reactions involved. (NCERT Exemplar Problem)

Solution: The compound A is diborane which reacts with NMe_3 to form adduct $BH_3.NMe_3$ (B). The hydrolysis of compound A gives boric acid, H_3BO_3 (C) and H_2 gas. The reactions are :

$$\underset{(A)}{B_2H_6} + NMe_3 \longrightarrow \underset{(B)}{B_2H_6.NMe_3}$$

$$B_2H_6 + 6H_2O \longrightarrow \underset{\text{Boric acid}\ (C)}{2H_3BO_3} + 6H_2$$

❑ Example 14.

When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities. **N.C.E.R.T.**

Solution: Since the metal X reacts with sodium hydroxide to form a white ppt (A), which dissolves in excess of NaOH to form a soluble complex (B), metal X is aluminium. The reactions are :

$$\underset{(X)}{2Al} + 3NaOH \longrightarrow \underset{\text{White ppt}\ (A)}{Al(OH)_3} + 3Na^+$$

$$\underset{(A)}{Al(OH)_3} + NaOH \longrightarrow \underset{\text{Sodium tetra hydroxoaluminate Soluble (B)}}{Na^+\,[Al(OH)_4]^-}$$

Compound (A) is amphoteric in nature and therefore, is soluble in dil HCl to form compound C, which must be $AlCl_3$.

$$\underset{(A)}{Al(OH)_3} + 3HCl \longrightarrow \underset{\text{Aluminium chloride}\ (C)}{AlCl_3} + 3H_2O$$

Compound (A) on heating gives (D) which is alumina, which is used to extract metal.

$$2Al(OH)_3 \longrightarrow \underset{(D)}{Al_2O_3} + 3H_2O$$

❑ Example 15.

Suggest reasons why the B—F bond lengths in BF_3 (130pm) and BF_4^- (143 pm) differ.

Solution: BF_3 is a planar molecule in which B is sp^2 hybridised. It has empty 2*p*-orbital. Because of similar sizes of B and F, back bonding occurs in which a lone pair is transferred from F to empty *p*-orbital of B forming $p\pi$-$p\pi$ bond. As a result, B–F acquires some double bond character. On the other hand, in BF_4^- ion, B is sp^3 hybridised and forms four B–F single bonds. It does not have vacant *p*-orbital available to accept the electrons from F atom and hence in BF_4^-, the B–F bond is purely single bond. Since double bond is shorter than single bond, therefore, the B–F bond length in BF_3 is shorter (130pm) than B–F bond length in BF_4^- (143 pm).

Practice Problems

1. What is the formula of colemanite ?
2. Are all the B—H bonds in diborane equivalent ?
3. What is the basicity of orthoboric acid ?
4. Name two ions which can be detected by borax bead test.
5. What are the basic units of the larger structure of orthoboric acid? How are they bonded ?
6. Is BF_3 a Lewis acid or a Lewis base ?
7. Why are boron halides called Lewis acids ?
8. What is the structure of BO_3^{3-} ion ?
9. What compounds are formed on heating boric acid ?
10. What is the oxidation state of boron in orthoboric acid ?

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Answers to Practice Problems

1. $Ca_2B_6O_{11}$
2. No, there are two types of bonds in diborane; two electron normal bonds and three centred two electron bonds.
3. Monobasic.
4. Ni^{2+}, Co^{2+}
5. BO_3^{3-} ions, bonded through hydrogen bonds.
6. Lewis acid.
7. Because they can accept electron pairs.
8. Trigonal planar.
9. HBO_2, $H_2B_4O_7$ and B_2O_3.
10. + 3.

add on

Conceptual Questions 1

CONCEPTUAL QA

Q.1. What is the oxidation state of boron in boric acid ? What is the basicity of this acid ?

Ans. Boric acid is H_3BO_3.
Oxidation state of boron = +3
Boric acid is monobasic.

Q.2. How does sodium hydride react with diborane ?

Ans. Sodium borohydride is formed.

$$2NaH + B_2H_6 \xrightarrow{\text{Heat}} 2NaBH_4$$

Q.3. Gallium has higher ionization enthalpy than aluminium. Explain why ?

Ans. Gallium has higher ionization enthalpy than aluminium because of higher effective nuclear charge. This is due to additional ten 3*d* electrons which do not screen the nuclear charge effectively so that the outer electrons are more strongly held.

Q.4. Molten aluminium bromide is a poor conductor of electricity. Explain.

Ans. Aluminium bromide is predominantly covalent compound. Even in the molten state it does not have ions which can conduct electricity.

Q.5. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution (ionisation enthalpy for Al = 5137 kJ mol^{-1}, $\Delta H_{hydration}$ of Al^{3+} = – 4655 kJ mol^{-1}) and $\Delta H_{hydration}$ of Cl^- = – 381 kJ mol^{-1}.

Ans. The energy released during hydration of Al^{3+} and $3Cl^-$ ions = – 4655 + 3(– 381) = – 5808 kJ mol^{-1}.
The energy released during hydration is greater than the ionisation enthalpy for Al (5137 kJ mol^{-1}).
Hence $AlCl_3$ will be ionic in solution.

Q.6. Boron forms no compounds in unipositive state but thallium in unipositive state is quite stable.

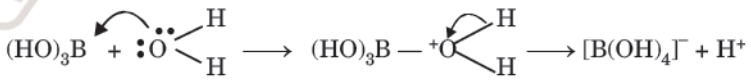
Ans. Boron has electronic configuration, $2s^2\ 2p^1$ and therefore forms compounds in trivalent state. However, thallium prefers to form compounds in +1 oxidation state rather than in +3 oxidation state as suggested by its group number. This is due to inert pair effect. According to this effect, the $6s^2$ electrons in the case of heavy metals preferably do not take part in bonding.

Q.7. Why is B–X bond distance in BX_3 shorter than the theoretically expected value ?

Ans. This is due to $p\pi$–$p\pi$ back bonding of the fully filled *p*-orbital of halogen (X) into the empty *p*-orbital of boron.

Q.8. Is boric acid a protic acid ? Explain. *N.C.E.R.T.*

Ans. Boric acid is not a protic acid because it does not ionise in water to give a proton. But it acts as a Lewis acid by accepting electrons from hydroxide ion :



or $B(OH)_3\,(aq) + 2H_2O \longrightarrow [B(OH)_4]^-(aq) + H_3O^+(aq)$

Thus, boric acid acts as Lewis acid because it reacts with OH^- (Lewis base) ions rather than acting as a Bronsted acid.

Q.9. How can you explain the higher stability of BCl_3 as compared to $TlCl_3$? *N.C.E.R.T.*

Ans. Boron exhibits +3 oxidation state and can form stable BCl_3. Thallium shows oxidation state of +3 as well as +1 but +1 oxidation state is predominant than +3 because of inert pair effect. Therefore. $TlCl_3$ is not stable. It can form stable TlCl.

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Q.10. Explain amphoteric character of aluminium.

Ans. Aluminium reacts with acids as well as alkalies and therefore, shows amphoteric character.

$$2Al\,(s) + 6HCl(aq) \longrightarrow 2Al^{3+}\,(aq) + 6Cl^{-}(aq) + 3H_2(g)$$

$$2Al(s) + 2NaOH(aq) + 6H_2O\,(l) \longrightarrow 2Na^{+}[Al(OH)_4]^{-}(aq) + 3\,H_2(g)$$

Sodium tetrahydroxoaluminate (III)

Q.11. Why do trihalides of Group 13 elements fume in the moist air ?

Ans. They are hydrolysed by water forming hydrogen halides.

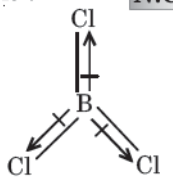
$$MX_3 + 3H_2O \longrightarrow M(OH)_3 + 3HX.$$

Q.12. Explain why aluminium, though electropositive metal, finds extensive use as a structural material.

Ans. Aluminium is electropositive metal and reacts with oxygen (or air) to form a hard protective layer of Al_2O_3 which protects it from further action. Therefore, it becomes passive and is extensively used as a structural material.

Q.13. If B–Cl bond has a dipole moment, why does BCl_3 has zero dipole moment ? ***N.C.E.R.T.***

Ans. BCl_3 molecule has a symmetrical trigonal structure in which three B–Cl bonds are oriented at an angle of 120° to one another. The three bonds lie in one plane and the dipole moments of these bonds cancel one another giving net dipole moment of zero.



$\mu = 0$

Q.14. Why does gallium undergo disproportionation reactions ?

Ans. Gallium shows both +1 and +3 oxidation states due to inert pair effect. However, its +3 oxidation state is more stable than +1 oxidation state. Therefore, +1 gallium is less stable than +3 gallium and hence undergoes disproportionation to form gallium and more stable +3 gallium ions in aqueous solution as shown below :

Reduced

$$\overset{+1}{3Ga\,X(s)} \longrightarrow \overset{0}{2Ga(s)} + \overset{+3}{Ga^{3+}\,(aq)} + 3X^{-}(aq)$$

Oxidised

or $3Ga^{+}\,(aq) \longrightarrow 2Ga(s) + Ga^{3+}\,(aq)$

Q. 15. Complete the following reactions :

(*i*) $NaBH_4 + I_2 \longrightarrow$

(*ii*) $B(OH)_3 + C_2H_5OH \xrightarrow[H_2SO_4]{Conc.}$

(*iii*) $NaBO_2 + CO_2 \longrightarrow$

Ans. (*i*) $2NaBH_4 + I_2 \xrightarrow{Diglyme} B_2H_6 + 2NaI + H_2$

(*ii*) $B(OH)_3 + 3C_2H_5OH \xrightarrow{Conc.\ H_2SO_4} B(OC_2H_5)_3 + 3H_2O$

(*iii*) $4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$

Q.16. Unlike In^{+}, Tl^{+} is more stable with respect to disproportionation.

Ans. Both In and Tl can show oxidation states of + 1 and + 3. The + 1 oxidation state of Tl is more stable than its + 3 oxidation state because of inert pair effect. But + 3 oxidation state of In is more stable than its + 1 oxidation state. Therefore, in aqueous solution, less stable In^{+} undergoes disproportionation to form more stable In^{3+} but Tl^{+} being more stable does not undergo disproportionation to form Tl^{3+}.

$$3\,In^{+}\,(aq) \xrightarrow{Disproportionation} 2\,In(s) + In^{3+}(aq)$$

$3\,Tl^{+}\,(aq) \longrightarrow$ does not undergo disproportionation.

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GROUP 14 ELEMENTS CARBON FAMILY

The group 14 of the periodic table contains five elements : **carbon** (C), **silicon** (Si), **germanium** (Ge), **tin** (Sn) and **lead** (Pb). This group is known as **carbon family.**

OCCURRENCE

Carbon occurs both as the free element (coal, graphite or diamond) and in the combined form (mainly as carbonates of Ca, Mg and other electropositive elements). It also occurs as CO_2, an important constituent of atmosphere (0.03%). Carbon is **seventeenth** in order of abundance in the earth's crust. It also occurs widely as hydrocarbons (natural gas, petroleum). Its combination with other elements such as dihydrogen, dioxygen, chlorine and sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is the branch of chemistry consisting of compounds of carbon. Naturally occurring carbon contains two stable isotopes ^{12}C and ^{13}C. In addition to these, a third isotope of carbon, ^{14}C is also present which is radioactive and has half life 5770 years and is used for radiocarbon dating for determining the age of earth, fossils, etc.

Silicon is the **second most abundant element** (about 27.7% by mass) **in the earth's crust after oxygen** (about 45.5 mass%) as silica (sand or quartz) and silicates. In silicates, $[SiO_4]$ unit may occur individually as groups or be linked to form chains, rings, sheets or three dimensional frameworks. Silicon is very important component of ceramics, glass and cement.

Germanium occurs rarely. Germanium minerals are extremely rare but the element is distributed in trace amounts in coal and zinc concentrates. Tin occurs mainly as **cassiterite**, SnO_2 and lead is found as **galena**, PbS. Other ores of lead are **anglesite** ($PbSO_4$) and **cerussite** ($PbCO_3$). Small quantities of lead ores occur in Rajasthan. The abundance of the elements in the earth's crust by weight is given below :

Element	Abundance in earth's crust (ppm)	Relative abundance
C	180	17
Si	2.77×10^5	2
Ge	1.5	54
Sn	2.1	49
Pb	13	36

GENERAL CHARACTERISTICS OF GROUP 14 ELEMENTS

A. Electronic Configurations

The atoms of these elements have four electrons in the outermost shell, two in *s* and two in *p* sub-shell. The general electronic configuration of this group may be expressed as ns^2np^2. The electronic configuration of the atoms of this group are given in Table 5.

Table 5. Electronic configuration of group 14 elements.

Element	Symbol	Atomic no.	Electronic configuration
Carbon	C	6	[He] $2s^2\ 2p^2$
Silicon	Si	14	[Ne] $3s^2\ 3p^2$
Germanium	Ge	32	[Ar] $3d^{10}\ 4s^2\ 4p^2$
Tin	Sn	50	[Kr] $4d^{10}\ 5s^2\ 5p^2$
Lead	Pb	82	[Xe] $4f^{14}5d^{10}\ 6s^2\ 6p^2$

B. Atomic and Physical Properties

The common physical constants of group 14 elements are given in Table 6.

Table 6. Some physical constants of group 14 elements.

	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Atomic mass	12.01	28.09	72.60	118.71	207.2
Atomic radius (pm)	77	118	122	140	146
Ionic radius (pm) M^{4+}	—	40	53	69	78
M^{2+}	—	—	73	118	119
Ionisation enthalpy (kJ mol^{-1})					
IE_1	1086	756	761	708	715
IE_2	2352	1577	1537	1411	1450
IE_3	4620	3228	3300	2942	3081
IE_4	6220	4354	4409	3929	4082
Electronegativity	2.5	1.8	1.8	1.8	1.9
Density (g cm^{-3})	3.51 (for diamond) 2.22 (for graphite)	2.34	5.32	7.26 (for β-form)	11.34
m.p. (K)	4373	1693	1218	505	600
b.p. (K)	—	3350	3123	2896	2024
Electrical resistivity (ohm cm at 293 K)	$10^{14} - 10^{16}$	50	50	10^{-5}	2×10^{-5}

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1. Atomic radii

The atomic radii of group 14 elements are less than the corresponding elements of group 13.

The atomic radii of group 14 elements increase down the family.

Explanation. The decrease in atomic radii is due to the increase in effective nuclear charge on going from group 13 element to group 14 element within the same period. As a result, the outermost electrons are attracted more strongly towards the nucleus and therefore, atomic radius decreases. Within the group, the atomic radii increase on going down the group, due to the increase in the number of electron shells.

It may be noted that the increase in atomic radii from Si onwards is small. This is due to the presence of completely filled *d*-and *f*-orbitals which have relatively ineffective shielding of the valence electrons.

2. Ionisation enthalpies

The first ionisation enthalpies of these elements are higher than the corresponding members of group 13 elements.

Explanation. The higher ionisation enthalpies are due to the higher nuclear charge and smaller size of atoms of group 14 elements.

While moving down the group, the ionisation enthalpies decrease. The first ionisation enthalpies ($\Delta_i H_1$) of elements of group 14 follow the order :

$$C > Si > Ge > Sn < Pb$$

This is due to increase in atomic size and screening effect which overweigh the effect of increase in nuclear charge. Therefore, the outermost electron becomes less and less tightly held by the nucleus and ionisation enthalpy decreases. The observed small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is due to the combined effects of poor shielding effect of intervening *d*-electrons in Ge and Sn and *d* and *f* orbitals in Pb and the increased atomic size of the elements.

3. Melting and boiling points

The atoms of this group form covalent bonds with each other and therefore, there are strong binding forces between their atoms in both solid and liquid states. Consequently, *the melting and boiling points of group 14 elements are much higher in comparison to group 13 elements.* On moving down the group, the melting and boiling points decrease.

4. Metallic character

Due to large ionisation enthalpies, the elements of this group are *less metallic* than the elements of group 13. On moving down the group, the metallic character increases from carbon to lead. For example, *carbon is typical non-metal, silicon also behaves as non-metal,* but in certain physical properties, it behaves as a semi-metal. Germanium is metalloid while tin and lead are typical metals.

C Non-metal
Si Non-metal
Ge Metalloid
Sn Metal
Pb Metal

METALLIC CHARACTER INCREASES

C. Oxidation State

The general valence shell electronic configuration of elements of group 14 is ns^2np^2. Therefore, these elements can achieve noble gas configuration either by losing or gaining four electrons forming M^{4+} and M^{4-} ions. Since the sum of first four ionisation enthalpies of carbon is very high, it is not usually available in chemical reactions and therefore, C^{4+} ions are not easily formed.

On the other hand, carbon cannot take up four electrons to form C^{4-} ion. This process is also energetically unfavourable because it requires a large amount of energy for adding four electrons. Therefore, the compounds in +4 oxidation state are generally covalent in nature. However, on moving down the group the tendency to form covalent compounds decreases and the tendency to form ionic compounds increases. Thus, the elements of group 14 show tetravalency by sharing four of its valence electrons. Therefore, they have oxidation state of +4.

In addition, Ge, Sn and Pb also show +2 oxidation state. It has been observed that on going down the group, the +2 oxidation state becomes more stable : Ge < Sn < Pb. For example, **for lead compounds, + 2 oxidation state is more predominant.** This is due to inability of *s*- electrons of the valence shell of tin and lead to participate in bonding. In other words, the pair of *s* electrons, 6*s* in lead, behaves as inert. This is known as **inert pair effect.**

The relative stabilities of these two oxidation states vary down the group. Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 oxidation state and only a few in +2 oxidation state. Tin forms compounds in both oxidation states +4 and +2.

These elements in + 2 oxidation state can act as reducing agents while in + 4 oxidation state they can act as oxidising agents.

Reducing agent $M^{2+} \longrightarrow M^{4+} + 2e^-$

Oxidising agent $M^{4+} + 2e^- \longrightarrow M^{2+}$

For example, Sn(II) salts such as $SnCl_2$ are widely used as reducing agents.

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$
$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

On the other hand, lead compounds in +2 oxidation state are more stable and in +4 oxidation state behave as strong oxidising agents.

For example, Pb (IV) salts such as lead tetraacetate $Pb(OCOCH_3)_4$ and PbO_2 are widely used as oxidising agents.

$$PbO_2 + 4HCl\ (conc.) \xrightarrow{Heat} PbCl_2 + Cl_2 + 2H_2O$$

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \\ \text{Ethylene glycol} \end{array} + Pb(OCOCH_3)_4 \xrightarrow{Heat} 2HCHO + Pb(OCOCH_3)_2 + 2CH_3COOH$$

Formaldehyde Lead acetate

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In the tetravalent state, the number of electrons around the central atom in a molecule (e.g., C in CCl_4) is eight. Therefore, these are regarded as **electron precise molecules** and hence neither act as ***electron acceptors*** or ***electron donors***. Although carbon cannot extend its covalence more than four, other elements of this group can do so because of the presence of *d*-orbitals in them.

C. Chemical Properties

The elements in this group are relatively unreactive, but reactivity increases down the group. The M(II) oxidation state becomes increasingly stable on descending the group. General chemical properties of group 14 elements are :

1. Reactivity towards oxygen

All the elements of group 14, when heated in oxygen form oxides. They generally form two types of oxides i.e. **monoxides** (MO) and **dioxides** (MO_2). SiO exists only at high temperatures. Besides monoxides and dioxides, lead also forms another oxide called *trilead tetroxide* or *red lead* (Pb_3O_4). It is formed by heating PbO (litharge) with excess of air or O_2 at 673K.

$$6PbO + O_2 \xrightarrow{673K} 2Pb_3O_4$$

(*i*) **Monoxides.** All the elements of this group form monoxides of the general formula MO such as CO, SiO, GeO, SnO and PbO. *Among monoxides, CO is neutral, GeO is distinctly acidic while SnO and PbO are amphoteric.*

Since +4 oxidation state of carbon is the most stable, therefore, among the monoxides of group 14, *CO is the strongest reducing agent.* Therefore, it is used in the extraction of many metals from their oxides.

$$ZnO + CO \xrightarrow{Heat} Zn + CO_2$$

$$Fe_2O_3 + 3CO \xrightarrow{Heat} 2Fe + 3CO_2$$

(*ii*) **Dioxides.** All the members of the family form dioxides with the molecular formula MO_2 *e.g.* CO_2, SiO_2, GeO_2, SnO_2, PbO_2. These dioxides differ markedly in their structures and properties. Carbon dioxide is a gas.

On the other hand, silicon dioxide called *silica* consists of continuous lattice of silicon and oxygen connected by covalent bonds (discussed later, Fig. 12).

Solid carbon dioxide is known as **dry ice**. It is soft, white snow like substance and looks like ice. However, it does not wet a piece of cloth or paper because it sublimes without melting. On the other hand, ordinary ice wets a piece of cloth on melting since it does not sublime. Solid carbon dioxide is used as a refrigerant under the commercial name **drikold.**

Among dioxides, CO_2, SiO_2 are acidic, GeO_2 is also acidic but less acidic than SiO_2 whereas SnO_2 and PbO_2 are amphoteric.

Being acidic, CO_2, SiO_2 and GeO_2 react with bases.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O$$

$$GeO_2 + 2NaOH \longrightarrow \underset{\text{Sodium germanate}}{Na_2GeO_3} + H_2O$$

The dioxides SnO_2 and PbO_2 are *amphoteric*. For example, SnO_2 reacts with acids as well as alkalies.

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$

$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

Similarly,

$$PbO_2 + 2NaOH \longrightarrow \underset{\text{Sodium plumbate}}{Na_2PbO_3} + H_2O$$

$$PbO_2 + 4HCl \xrightarrow{273K} PbCl_4 + 2H_2O$$

PbO_2 is a powerful **oxidising agent**. Therefore, it reacts with conc. HNO_3 or H_2SO_4 to evolve oxygen and oxidises HCl to Cl_2.

$$2PbO_2 + 4\,HNO_3 \xrightarrow{Heat} 2Pb(NO_3)_2 + 2H_2O + O_2$$

$$2PbO_2 + 2H_2SO_4 \xrightarrow{Heat} 2PbSO_4 + 2H_2O + O_2$$

$$PbO_2 + 4HCl \xrightarrow{Heat} PbCl_2 + Cl_2 + H_2O$$

2. Reactivity towards water

Carbon, silicon and germanium are not affected by water. However, tin reacts with steam to form SnO_2 and dihydrogen gas.

$$\underset{\text{Steam}}{Sn + 2H_2O} \xrightarrow{Heat} SnO_2 + 2H_2$$

Lead is not affected by water probably because of a protective oxide film.

3. Reactivity towards halogens

The elements of group 14 form tetrahalides of the formula EX_4 and dihalides (EX_2) (X = F, Cl, Br, I).

Tetrahalides. All the elements form tetrahedral halides, MX_4, which are mostly covalent. Except carbon, all other members react directly with halogens under suitable conditions to form tetrahalides. Si and Ge react readily with all the halogens forming volatile halides, SiX_4 and GeX_4. Sn and Pb are less reactive. Sn reacts with Cl_2 and Br_2 in cold and with F_2 and I_2 on warming, forming SnX_4. Pb reacts with F_2 in the cold forming PbF_2 and with chlorine forming $PbCl_2$. These tetrahalides have tetrahedral structure. The central atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape.

Most of the tetrahalides are covalent in nature. Exceptions are SnF_4 and PbF_4, which are ionic in nature. PbI_4 does not exist because Pb—I bond initially formed during the reaction does not release sufficient energy to unpair $6s^2$ electrons and excite one of them

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to higher orbitals to have four electrons around the lead atom. The nonexistence of PbI_4 may also be explained due to strong oxidising power of Pb (IV) and strong reducing power of I^-.

The chlorides except CCl_4 are hydrolysed readily by water. For example,

$$SiCl_4 + H_2O \longrightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$

$$SnCl_4 + 2H_2O \longrightarrow SnO_2 + 4HCl$$

$$CCl_4 + H_2O \longrightarrow \text{No reaction}$$

Hydrolysis of silicon tetrafluoride gives silica and fluorosilicic acid.

$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + \underset{\text{Fluorosilicic acid}}{2H_2SiF_6}$$

Carbon tetrahalides do not form complexes because carbon does not have vacant *d*–orbitals in its valence shell and therefore, cannot increase its coordination number. On the other hand, the halides of other elements form complexes due to the availability of vacant *d*-orbitals in the valence shell. These can increase the coordination number to six. In other words, they behave as ***Lewis acids*** but CCl_4 does not.

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

$$SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{2-}$$

$PbCl_4$ and $PbBr_4$ are unstable while PbI_4 is not known.

Dihalides. Carbon does not form dihalides while the other elements form dihalides, MX_2. **The stability of dihalides increases down the group.** The stability of dihalides follows the sequence :

$$CX_2 << SiX_2 << GeX_2 << SnX_2 < PbX_2.$$

For example, PbX_2 is more stable than PbX_4. On the other hand, GeX_4 is more stable than GeX_2. Tin(II) chloride is obtained by dissolving tin in conc. HCl. When the solution is cooled, crystals of $SnCl_2.2H_2O$ (dihydrate) separate out. Anhydrous $SnCl_2$ is prepared by heating tin in a current of HCl vapour.

$SnCl_2$ is used as a reducing agent in acid solution. For example, it reduces Fe^{3+} to Fe^{2+} state as :

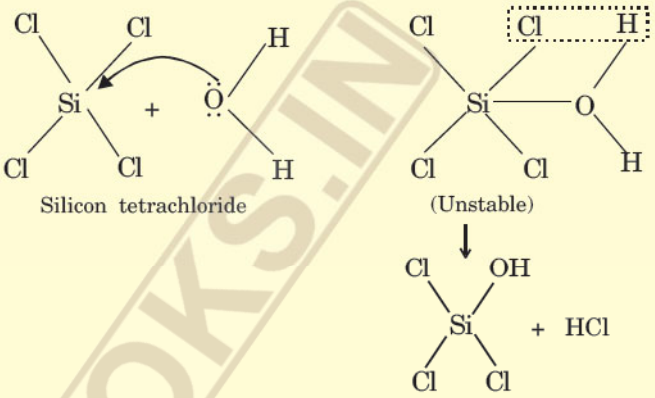
$$2Fe^{3+} + Sn^{2+} \longrightarrow Sn^{4+} + 2Fe^{2+}$$

Lead (II) halides are formed by adding halide ions to soluble lead salt :

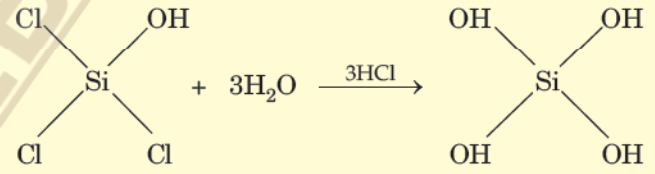
$$Pb^{2+} + 2X^- \longrightarrow PbX_2 \ (X = F, Cl, Br \text{ or } I)$$

Pb (II) halides are colourless solids except PbI_2 which is yellow. These are sparingly soluble in water. In qualitative analysis, Pb^{2+} ion is tested as $PbCl_2$ or PbI_2.

CCl_4 cannot be hydrolysed while $SiCl_4$ can be easily hydrolysed. This can be easily explained on the basis of absence of *d*-orbitals in the valence shell of carbon. Carbon has only *s* and *p*-orbitals. As a result, carbon cannot increase its coordination number beyond four and therefore, it cannot accept electrons from water molecules. On the other hand, $SiCl_4$ is readily hydrolysed by water because silicon has vacant 3*d* orbitals in its outermost shell. As a result, silicon extends its coordination number beyond four. The vacant 3*d* orbitals of silicon accept electrons from water and $SiCl_4$ can be hydrolysed as shown below :



One Cl atom is replaced in $SiCl_4$ by OH group forming $SiCl_3$.OH. The process continues till all the 4 Cl atoms are replaced forming $Si(OH)_4$ or H_2SiO_3 . H_2O (hydrated silicic acid). Thus,



Silicic acid
or $H_2SiO_3.H_2O$

4. Reactivity with acids and alkalies

C, Si and Ge are unaffected by acids. Sn dissolves in dilute HNO_3 forming $Sn(NO_3)_2$. Lead dissolves slowly in dilute HCl forming the sparingly soluble $PbCl_2$ but quite readily in dil. HNO_3 forming $Pb(NO_3)_2$ and oxides of nitrogen,

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$Pb + 4HNO_3 \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$

Lead also dissolves in organic acids (e.g., oxalic acid, acetic acid, citric acid, etc).

$$Pb + 2CH_3COOH + \frac{1}{2}O_2 \longrightarrow \underset{\text{Lead acetate}}{(CH_3COO)_2Pb} + H_2O$$

Lead does not dissolve in dil H_2SO_4 because a surface coating of $PbSO_4$ is formed.

Graphite reacts with hot concentrated HNO_3 forming mellitic acid $[C_6(COOH)_6]$ and with a mixture of HF and HNO_3 forming graphite oxide. On the other hand, Si gets oxidized and fluorinated by concentrated, HF, HNO_3 mixture. Ge dissolves in hot concentrated H_2SO_4 as well as HNO_3. Sn dissolves in

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several concentrated acids. Pb does not dissolve in concentrated HCl because a surface coating of $PbCl_2$ is formed. However, powdered lead is readily dissolved by boiling hydrochloric acid due to the formation of soluble complex, $H_2[PbCl_4]$.

$$Pb + 2HCl \longrightarrow PbCl_2 + H_2$$
$$PbCl_2 + 2HCl \longrightarrow \underset{\text{Chloroplumbous acid}}{H_2[PbCl_4]}$$

Carbon is unaffected by alkalies. Si reacts slowly with cold aqueous solution of NaOH and readily with hot solutions forming silicates.

$$Si + 2KOH + H_2O \longrightarrow K_2SiO_3 + 2H_2$$

It also dissolves in fused sodium carbonate displacing carbon.

$$Na_2CO_3 + Si \longrightarrow Na_2SiO_3 + C$$

Sn and Pb are slowly attacked by cold alkali and rapidly by hot alkali forming stannates and plumbates.

$$Sn + 2NaOH + 4H_2O \longrightarrow \underset{\text{Sodium stannate}}{Na_2[Sn(OH)_6]} + 2H_2$$

$$Pb + 2NaOH + 4H_2O \longrightarrow \underset{\text{Sodium plumbate}}{Na_2[Pb(OH)_6]} + 2H_2$$

This also shows amphoteric character of Sn and Pb.

5. Formation of hydrides

All the elements except lead of group 14 form covalent hydrides of the type MH_4. The number of hydrides, their thermal stability and their ease of formation decreases from C to Pb.

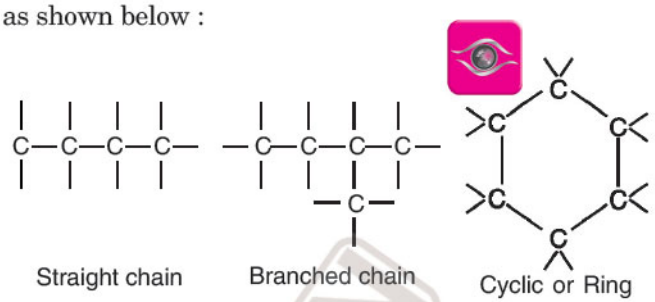
Carbon forms a number of cyclic and acyclic hydrides known as **hydrocarbons.** The common are alkanes (having general formula, C_nH_{2n+2}), alkenes (having general formula C_nH_{2n}) alkynes (having general formula, C_nH_{2n-2}) and aromatic hydrocarbons. Silicon forms only a limited number of hydrides known as ***silanes*** having general formula Si_nH_{2n+2} (n = 1 – 8). The silanes resemble hydrocarbons in many properties.

Germanium hydrides are called **germanes** having the general formula Ge_nH_{2n+2} (n = 1 – 5). Tin forms two hydrides, SnH_4 and Sn_2H_6. On the other hand, lead is known to form only one hydride, plumbane PbH_4, which is difficult to prepare.

D. Unique Character of Carbon

Carbon being the first member of group 14 shows many unique characteristics as described below :

1. Catenation. This is one of the remarkable property of carbon to form bonds with itself. *This property of forming bonds with atoms of the same element is called* **catenation.** Carbon shows maximum catenation in its group. On moving down the group 14, the catenation tendency decreases. Because of catenation, carbon atoms can link with each other to form a large variety of compounds such as *linear chains, branched chains* and *rings* of different sizes and lengths as shown below :



The tendency to catenation depends upon the strength of M—M bond. As we go down the group the strength of M—M bond decreases due to increase in size of the atom. The bond enthalpies of various bonds are :

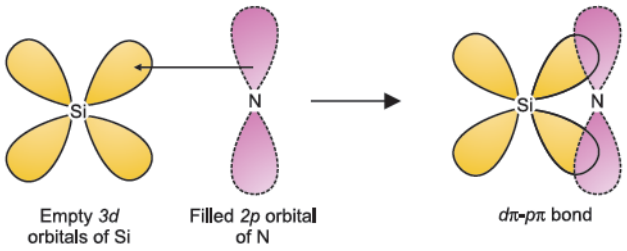
Bond	Bond enthalpy (kJ mol^{-1})
C — C	348
Si — Si	297
Ge — Ge	260
Sn — Sn	240

Thus, the **tendency to catenation decreases as : C >> Si > Ge ≈ Sn > Pb.**

2. Tendency to form multiple bonding. Carbon has also unique tendency to form stable multiple bonds (double and triple) with itself and with other atoms of small size and high electronegativity. For example,

C=C, C≡C, C=O, C=S and C≡N

In these compounds there are $p\pi$–$p\pi$ bonding. However, silicon and other elements of the group have vacant d–orbitals in their valence shell. As a result, silicon can form $d\pi$–$p\pi$ double bond with elements like O and N due to the availability of vacant d–orbitals in its outermost shell. This bond is formed by the donation of electron pair from filled 2p orbitals of N or O to the vacant 3d orbitals of Si. It is called **back bonding.**



The presence of $d\pi$—$p\pi$ bond helps to explain the bonding in *trimethylamine* $(CH_3)_3N$ and *trisilylamine* $N(SiH_3)_3$.

The compounds $(CH_3)_3N$ and $(SiH_3)_3N$ have different structures. In trimethylamine, the N atom involves sp^3 hybridisation having one lone pair in one of its tetrahedral position. The geometry is regarded as **pyramidal** [Fig. 9(a)]. In the trisilylamine, sp^2 hybridisation takes place and the molecule has **trigonal planar** geometry [Fig. 9(b)].

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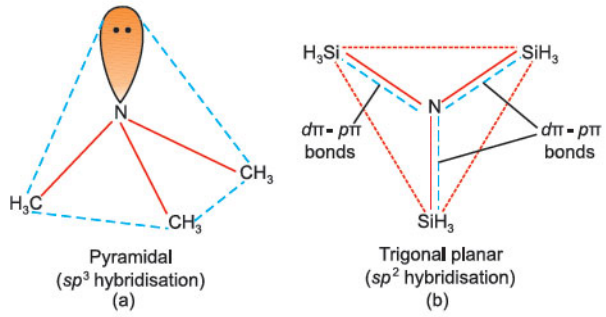


Fig 9. Structure of $(CH_3)_3N$ and $(SiH_3)_3$ N involving $d\pi$—$p\pi$ back bonding in $(SiH_3)_3N$.

The lone pair is present in unhybridized *p*–orbital. This overlaps with empty *d*–orbitals on each of the three Si atoms and results in back $p\pi$–$d\pi$ bonding. Since the lone pair on nitrogen is involved in back bonding with vacant *d*–orbitals of silicon, N has no longer a lone pair of electrons. As a result, the molecule does not have donor properties. Its structure is plannar. Such type of $p\pi$—$d\pi$ bonding cannot occur in $(CH_3)_3$ N because carbon does not have *d*–orbitals.

ALLOTROPES OF CARBON

Elemental carbon exists in many allotropic forms. **Allotropic forms** or **allotropes** are

the different forms of the same element having different physical properties but almost similar chemical properties.

The phenomenon of existence of allotropic forms of an element is called **allotropy.**

Carbon exists in two types of allotropic forms :

1. Crystalline. Diamond and graphite are two crystalline forms of carbon having well defined structure.

2. Amorphous. There are many amorphous forms of carbon such as coal, wood charcoal, animal charcoal, lamp black, coke, gas carbon, etc.

Of these allotropic forms, diamond and graphite are the most important and are discussed below :

Structure of Diamond and Graphite

Diamond and graphite are two crystalline allotropic forms of carbon as shown in Fig. 9. Some of the important properties of these are :

(*i*) Diamond is denser than graphite. The density of diamond is 3.514 g cm^{-3} while that of graphite is 2.226 g cm^{-3}.

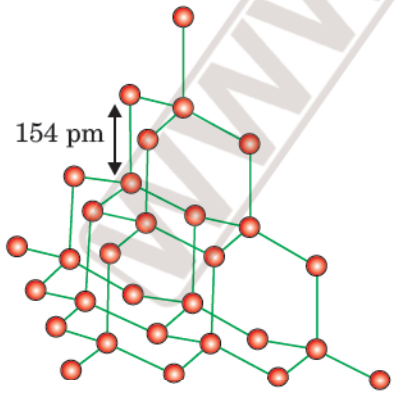
(*ii*) Diamond is hard while graphite is soft. Graphite has lubricating properties. On the other hand, diamond is the hardest substance known.

(*iii*) Diamond is a bad conductor of electricity while graphite is a good conductor of electricity.

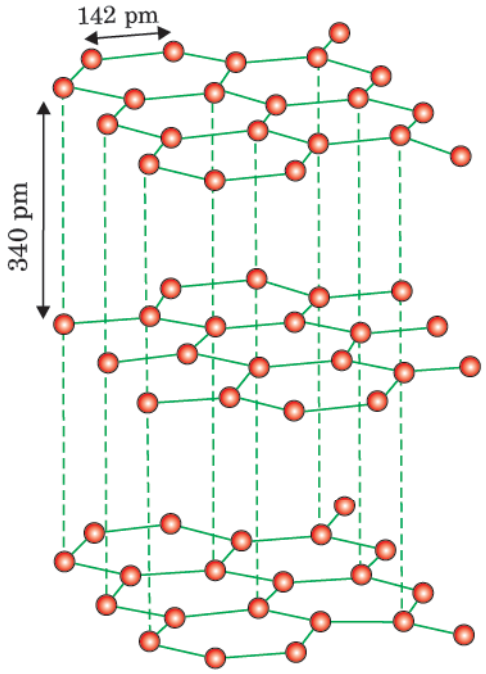
(*iv*) Diamond is extremely chemically unreactive whereas graphite is quite reactive.

The different properties of diamond and graphite can be easily explained on the basis of their structures as described below.

Structure of diamond. Diamond has a network structure consisting of a very large number of carbon



(*a*) Structure of diamond.



(*b*) Structure of graphite.

Fig. 10.

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atoms bonded to each other. Each carbon atom is sp^3 hybridised and is bonded to four other carbon atoms by single covalent bonds. The structure of diamond is shown in Fig 10 (*a*). It is clear from the figure that each carbon atom lies at the centre of a regular tetrahedron and the other four carbon atoms are present at the corners of the tetrahedron. In this structure all C—C bond lengths are equal to 154 pm. Therefore, there is a *three-dimensional network of strong covalent bonds* in diamond. This makes diamond an extremely hard crystal with very high melting point (3843 K).

Since all the valence electrons of carbon are strongly held in carbon-carbon bonds, diamond is a poor conductor of electricity.

Structure of graphite. In graphite, each carbon atom undergoes ***sp*² hybridisation** and is covalently bonded to three other carbon atoms by single bonds. The fourth electron on each carbon atom results in the formation of π bonds (not shown in figure). In this way, graphite consists of hexagonal rings in *two dimensions* [Fig. 10 (*b*)]. The C—C covalent distance in rings is 142 pm indicating strong bonding. These arrays of ring form layers. The layers are separated by a distance of 340 pm. The large distance between these layers indicates that only weak van der Waals forces hold these layers together. The weak van der Waals' forces which hold these layers together are responsible for soft nature of graphite.

Because of the weak van der Waals forces between layers, one layer can move over the other layer and this accounts for the slippery nature of graphite. Therefore, graphite is used as *lubricant*. The electrons forming π bonds in the rings of graphite are delocalised and are relatively free to move under the influence of electric field. Therefore, graphite is a good conductor of electricity.

Comparison of Properties of Diamond and Graphite on the Basis of Structural Differences

On the basis of structural differences, the important properties of diamond and graphite can be easily compared.

(*i*) Density. In the case of graphite the different layers are held together by relatively weak van der Waals' forces and the layers are about 340 pm distance apart. This distance of separation between layers is more than twice the carbon-carbon distance (154 pm) in diamond. Because of wide separation in structure of graphite, its density is lower than that of diamond.

(*ii*) Hard and soft nature. Diamond has three dimensional network of strong covalent bonds. It is very difficult to break extended covalent bonding and therefore, *diamond is the hardest substance on earth.* On the other hand, graphite has layer structure and the layers are held together by weak van der Waals' forces. Therefore, graphite cleaves easily between the layers and this explains its flaky appearance, softness and lubricating properties.

(*iii*) Conductivity. Graphite has delocalised π electrons which are relatively free to move under the influence of electric field. Therefore, graphite is a good conductor of electricity. However, in diamond all the valence electrons are involved in forming carbon-carbon bonds and does not have free electrons and, therefore, it is a bad conductor of electricity.

(*iv*) Reactivity. In diamond, all the four valencies of carbon are satisfied by bonds with other carbon atoms. Therefore, diamond is extremely unreactive at room temperature. Graphite, on the other hand, reacts more readily due to the presence of π bonds.

Uses of Diamond

(*i*) Due to its hardness, it is used for cutting glass, making bores for rock drilling and for making abrasives for sharpening hard tools.
(*ii*) Due to its brilliance, diamond is used in jewellery as a precious stone. When it is cut at certain angles and polished, brilliant light is refracted from its surfaces, which makes it a precious gem.
(*iii*) It is used for grinding and polishing hard materials.
(*iv*) Diamond is also used for making dies for drawing thin wires from metals.
(*v*) It is used in the manufacture of tungsten filaments for electric light bulbs.

Uses of Graphite

(*i*) Graphite is used in making electrodes.
(*ii*) It is used as a lubricant for heavy machines running at high temperature, where oil cannot be used as a lubricant.
(*iii*) It is used in the manufacture of crucibles which can withstand high temperatures.
(*iv*) Mixed with wax or clay, graphite is used for making lead pencils.
(*v*) Graphite is also used as a moderator for fast moving neutrons in atomic reactors.

Amorphous Forms of Carbon

Some important amorphous forms of carbon are :

(*i*) Coke. It is greyish black hard solid which is obtained by destructive distillation (strong heating in the absence of air) of coal. It is commonly used as a fuel in boilers, engines and it is also used in furnaces as a reducing agent in metallurgy.

(*ii*) Charcoal. It is a black, soft and highly porous substance. It can be obtained in three varieties :

(*a*) Wood charcoal. It is obtained by heating wood in a limited supply of air. It is highly porous and is therefore used as an adsorbent for gases and in making gas masks.

(*b*) Animal charcoal. It is obtained by destructive distillation of bones and is also known as bone black. It contains about 10% carbon. It is mainly used for decolourising sugar syrup in the manufacture of sugar and other organic substances.

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(c) Sugar charcoal. It is the *purest form of amorphous carbon* and is obtained by the action of concentrated sulphuric acid on cane sugar.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Sugar charcoal}}{12C} + 11H_2O$$

It is used as black pigment.

***(iii)* Lamp black.** It is a fine black powder and is obtained by burning oils (such as kerosene oil, turpentine oil, petroleum, natural gas, etc.) in a limited supply of air. It is mainly used for making printers ink, black paints and shoe polish. It is also used as a filler in making rubber tyres.

Fullerenes

Upto 1985, carbon was considered to have only two allotropes graphite and diamond. In 1985, scientists discovered a new family of carbon allotropes consisting of cluster of carbon atoms such as C_{32}, C_{50}, C_{60}, C_{70}, C_{84}, etc. These were called **fullerenes.** These were discovered by H.W. Kroto, R.F. Curl and R.E. Smalley. This exciting discovery has opened a new era in chemistry. The 1996 Noble Prize in chemistry was awarded to the above scientists for their discovery of fullerenes, the new form of carbon. Among these the allotrope having the molecular formula C_{60} is important. It is named Buckminster fullerene. It was named after the name of American architect Robert Buckminster Fuller, who designed 'geodesic domes' that exactly resembled with it.

Fullerenes are made by heating graphite in an electric arc in the presence of an inert atmosphere of helium or argon. The sooty material formed by the condensation of vapourised C_n small molecules consists of mainly C_{60} with small amount of C_{70} and traces of other fullerenes consisting of even number of C atoms upto 350 or more. C_{60} and C_{70} can be readily obtained by extraction with aromatic hydrocarbon solvents such as benzene, toluene and the individual members are separated by chromatographic separation over alumina. The purified fullerenes have very attractive colours.

The process may be represented as :

$$\text{Graphite} \xrightarrow[\text{He or Ar}]{\text{Electric arc}} \text{Vapourised carbon} \xrightarrow{\text{Condensation}} \text{Fullerene soot} \xrightarrow[\text{separation over alumina}]{\text{Chromatographic}} \underbrace{C_{60} + C_{70}}_{\text{Fullerenes}}$$

The structural determination of C_{60} molecule has shown that it is a perfect sphere and looks like a soccer–ball. Therefore, it is also popularly known as **bucky-ball** (Fig. 11). It consists of five and six membered carbon rings. It has highly symmetrical structure in which all the carbon atoms occupy

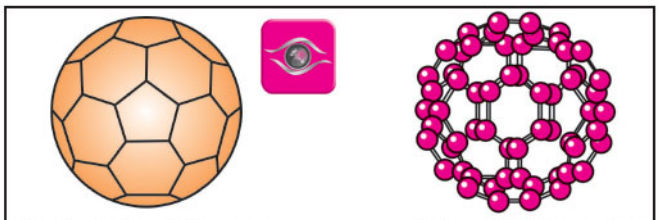

Fig. 11. Structure of fullerene.

identical positions. C_{60} fullerene molecule has 60 vertices and each one is occupied by one carbon atom. It has a geometry of truncated icosahedron having **20 hexagons** (six membered rings) and **12 pentagons** (five membered rings). Six membered rings are fused both to other six membered rings and five membered rings but five membered rings are connected to only six membered rings. In this case, all the carbon atoms are equivalent and they undergo sp^2 hybridisation. Each carbon atom forms three σ bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which give aromatic character to the molecule. The molecule has single and double bonds with C—C distance of 145.3 and 138.3 pm respectively.

C_{70} fullerene has **12 pentagonal and 25 hexagonal faces**. There are five types of carbon atoms and thus eight distinct types of C—C bonds which vary from 139 to 154 pm.

For example, thin films of C_{60} have mustard colour (dark brown in bulk) and solutions in aromatic hydrocarbons have beautiful magenta colour. Fullerenes differ from graphite and diamond in their solubilities. Being network solids, both graphite and diamond are insoluble in organic solvents. However, fullerenes dissolve in organic solvents to give coloured solutions. For example, a solution of C_{60} in toluene is purple whereas that of C_{70} is orange red.

Fullerene differs from diamond and graphite which form lattices whereas it forms discrete molecules. Being network solids both graphite and diamond are insoluble in liquid solvents. However, fullerene which is molecular can be dissolved in suitable organic solvents (such as benzene).

It is interesting to note that graphite is thermodynamically most **stable allotrope of carbon** and, therefore, $\Delta_f H^\circ$ of graphite is taken as zero. The standard enthalpy of formation ($\Delta_f H^\circ$) of diamond and fullerene are 1.90 and 38.1 kJ mol^{-1} respectively.

Thus, thermodynamically graphite is more stable than diamond because its enthalpy of formation is +1.90 kJ mol^{-1} lower than diamond at room temperature and atmospheric pressure.

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USES OF CARBON AND OTHER ELEMENTS

Uses of Carbon

Carbon is used extensively in its different forms. Coal is used as a fuel in boilers, engines, furnaces, etc. It is also used for the manufacture of coal gas, water gas, producer gas and synthetic petrol. It is largely used as a reducing agent in metallurgy. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Charcoal (activated) being porous is used as an excellent adsorbent to purify and deodorize sugar and other chemicals. It is also used to adsorb poisonous gases in gas masks and for removing offensive odour from the air used in air conditioning processes. It is also used in water filters to remove organic contaminators. Graphite being a good conductor of electricity is used for making electrodes in batteries and industrial electrolysis. Graphite fibres embedded in plastic material form high strength, light weight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. It is also used in steel making, metal foundries for crucibles, as a lubricant and in pencils etc. Crucibles made from graphite are inert to dilute acids and alkalies. It is also used as the moderator in the cores of gas cooled nuclear reactors to slow down neutrons. Diamonds (allotropes of carbon) are cut as gemstones and used in jewellery and other articles. It is measured in carats (1carat = 200 mg). It is also used for industrial purposes mainly for making drills or as an abrasive powder for cutting and polishing.

The important uses of different allotropic forms of carbon are given in Table 6.

Table 6. Uses of various allotropic forms of carbon.

Form of Carbon	Uses
Diamond	• due to its hardness, used for cutting glass, making bores for rock drilling, making abrasives • in jewellery as a precious stone, gem stone • for grinding and polishing • for making dyes for drawing thin wires from metals • in industry
Graphite	• steel manufacture (reducing agent) refractories • electrodes in electrolytic extraction of elements • lubricant for heavy machines • high temperature crucibles and high strength composite materials • moderator in nuclear reactors • for lead pencils
Coke	• fuel in boilers and engines • in furnaces as a reducing agent in metallurgy (steel manufacture)
Carbon black	• rubber industry as a filler • pigment in ink, paints and plastics
Activated charcoal	• decolourizing agent in sugar industry • purification of chemicals and gases by adsorption • as catalyst
Charcoal	• fuel • reducing agent

Uses of Silicon

Silicon is used as *n*-type or *p*-type semiconductors when doped with Group15 or Group13 element respectively. Silicon and germanium are extensively used in very pure forms in semiconductor devices, which are the basis of the whole electronic industry including computer hardware. Silicon is very important component of ceramics, glass and cement. Silicon is added to steel or iron as such or more usually in the form of ferrosilicon to increase its resistance to attack by acids. Very pure silicon is used to make computer chips. Its alloys such as *silicon bronze* and *manganese-silicon bronze* possess strength and hardness even greater than steel.

Uses of Germanium

Germanium has largest use in transistor technology, in making transistors and other semiconductor devices. It is transparent to infra red light and therefore is also used for making prisms and lenses and windows in infra red spectrometers and other scientific apparatus.

Uses of Tin

Because of low strength and high cost of **tin**, it is rarely used by itself but it is used for electroplating and as alloys. Tin plates obtained by electroplating steel with tin are extensively used for making cans, for food and drinks. It is used in the preparation of a number of important alloys such as **solder** (Sn/Pb), **bronze** (Pb/Cu/Sn), **babbitt** (Sn/Pb or Cu/Pb/Sn/Sb), **pewter** (Pb/Sn/Sb/Cu), **type metal** (Pb/Sn/Sb), etc.

Uses of Lead

Lead is used for making lead sheets, lead pipes, etc. It is also used for making telegraph and telephone wires which are to be burried in earth. It is used in

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storage batteries, making bullets. It is commonly used in making pigments like chrome yellow, chrome red, red lead, white lead, etc. Lead is also used for making important alloys such as type metal, solder, pewter, etc.

SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

Carbon combines with a variety of other elements to form binary compounds such as oxides, halides and carbides.

(1) Oxides of Carbon

Carbon burns in air or oxygen to form two oxides namely (*a*) carbon monoxide (CO) and (*b*) carbon dioxide (CO_2).

(*a*) Carbon monoxide (CO)

Preparation

(*i*) Carbon monoxide is prepared by incomplete combustion of carbon or carbon containing compounds in a limited supply of oxygen.

$$C(s) + \frac{1}{2}O_2(g) \xrightarrow{\text{Heat}} CO(g)$$

or $$2C(s) + O_2(g) \xrightarrow{\text{Heat}} 2CO(g)$$

Carbon monoxide is also present in exhaust gases from automobiles due to incomplete combustion of carbon or carbon compounds during burning of petrol or diesel.

(*ii*) Carbon monoxide is prepared by the reduction of oxides of heavy metals with carbon.

$$ZnO + C \longrightarrow Zn + CO$$

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

(*iii*) **Pure carbon monoxide** can be prepared on a **laboratory scale** by heating formic acid (HCOOH) with sulphuric acid at about 373 to 413 K. Sulphuric acid acts as a dehydrating agent.

$$HCOOH \xrightarrow[-H_2O]{H_2SO_4,\ 373-473K} CO$$

(*iv*) **On commercial scale,** carbon monoxide is prepared by passing steam over red hot coke. This reaction produces hydrogen also.

$$C(s) + H_2O(g) \xrightarrow{473-1273\ K} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$$

The mixture of CO and H_2 is called **water gas** or **synthesis gas.** When air is passed instead of steam, a mixture of CO and N_2 are formed. This mixture is called **producer gas**.

$$2C(s) + \underbrace{O_2(g) + 4N_2(g)}_{\text{Air}} \xrightarrow{1273\ K} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas}}$$

The water gas and producer gas are very important industrial fuels. Carbon monoxide present in water gas or producer gas can undergo further combustion forming carbon dioxide with the evolution of heat.

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)\ ;\quad \Delta_r H^\circ = -566\ kJ\ mol^{-1}$$

Carbon monoxide is also present in *volcanic gases, gases from the furnaces where coal is burnt, exhaust gases from automobile engines, fumes of tobacco, etc.*

Structure of carbon monoxide

The electron dot structure of carbon monoxide may be represented as :

$$:C::\ddot{O}: \text{ or } C{=}O$$

However, it is regarded as resonance hybrid of the following structures :

$$:C::\ddot{O}: \longleftrightarrow :\bar{C}:\!\!\overset{+}{:}\!O: \longleftrightarrow :\dot{\dot{C}}:\ddot{\underset{\cdot\cdot}{O}}:^{-}$$

The presence of a triple bond between C and O is supported by the fact that the carbon–oxygen bond length in CO is 113 pm which corresponds to carbon oxygen triple bond.

Properties

1. Carbon monoxide is colourless, odourless and is almost insoluble in water.

2. Toxic nature. It is highly toxic in nature. The toxic nature of CO is due to its ability to form a complex with haemoglobin in the red blood cells. Haemoglobin in the blood combines with oxygen and forms oxyhaemoglobin by a reversible reaction :

$$\text{Haemoglobin} + O_2 \rightleftharpoons \text{Oxyhaemoglobin}$$

Oxyhaemoglobin is formed in the lungs and is carried to the different cells where it gives its oxygen. However, CO forms complex with haemoglobin more strongly than oxygen. The CO complex with haemoglobin is about 300 times more stable than the oxygen-haemoglobin complex. Therefore, if CO is present, it will form stable compound with haemoglobin and this will destroy the oxygen carrying ability of the blood. As a result, blood will not take up oxygen easily, causing suffocation and finally death.

3. Combustibility. Carbon monoxide burns in air with a pale blue flame forming carbon dioxide.

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2 + \text{Heat}$$

4. Reducing character. It is a powerful reducing agent and reduces many metal oxides to metals. For example,

$$ZnO + CO \xrightarrow{\text{Heat}} Zn + CO_2$$

$$CuO + CO \xrightarrow{\text{Heat}} Cu + CO_2$$

$$Fe_2O_3 + 3CO \xrightarrow{\text{Heat}} 2Fe + 3CO_2$$

Carbon monoxide reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxides.

5. Formation of metal carbonyls. In carbon monoxide, there are one sigma and two π bonds between carbon and oxygen, $:C{\equiv}O:$. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated

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to form metal carbonyls. It combines with many transition metals such as nickel, iron, cobalt, etc. forming variety of compounds known as metal carbonyls. For example,

$$Ni + 4CO \xrightarrow{60\text{–}70^\circ C} \underset{\text{Nickel carbonyl}}{Ni(CO)_4}$$

$$Fe + 5CO \longrightarrow \underset{\text{Iron carbonyl}}{Fe(CO)_5}$$

6. Reaction with chlorine. Carbon monoxide readily combines with chlorine in sunlight to give carbonyl chloride, phosgene. Phosgene is a poisonous gas.

$$CO\,(g) + Cl_2\,(g) \longrightarrow \underset{\text{Phosgene}}{COCl_2\,(g)}$$

Uses of Carbon monoxide

(*i*) Carbon monoxide is used as an industrial fuel in the form of water gas and producer gas :

(*a*) **Water gas** is a mixture of carbon monoxide and hydrogen. It is obtained by passing steam over red hot coke.

$$C + H_2O\,(\text{steam}) \longrightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$

Water gas is also known as **synthesis gas or syn gas.**

(*b*) **Producer gas** is a mixture of carbon monoxide and nitrogen. It is prepared by passing air over a bed of red hot coke at about 1273 K.

$$2C + O_2 + 4N_2 \xrightarrow{1300\ K} \underbrace{2CO + 4N_2}_{\text{Producer gas}}$$

Both water gas and producer gas contain CO as their important component which can undergo further oxidation to form carbon dioxide and liberates enormous amount of heat. Therefore, these are used as important industrial fuels.

(*ii*) It is used in some metallurgical processes. For example, in the metallurgy of iron, it is used as a reducing agent.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

It is used in *Mond's process* for the purification of nickel by forming nickel carbonyl.

(*iii*) It is used in the manufacture of methyl alcohol, formic acid, etc.

(*iv*) Its compound with iron (iron carbonyl) is used in the manufacture of magnetic tapes for tape recorders.

(*b*) Carbon dioxide (CO_2)

Preparation

(*i*) Carbon dioxide is prepared by burning carbon, hydrocarbons or carbon monoxide in excess of air.

$$C + O_2 \xrightarrow{\text{Heat}} CO_2$$

$$CH_4 + 2O_2 \xrightarrow{\text{Heat}} CO_2 + 2H_2O$$

$$C_5H_{12} + 8O_2 \xrightarrow{\text{Heat}} 5CO_2 + 6H_2O$$

$$2CO + O_2 \xrightarrow{\text{Heat}} 2CO_2$$

(*ii*) In the **laboratory**, it is prepared by the action of dilute hydrochloric acid on carbonates such as $CaCO_3$.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

(*iii*) On an **industrial scale**, it is obtained as a by-product in some industrial processes such as manufacture of lime, manufacture of alcohol, etc.

$$\underset{\text{Limestone}}{CaCO_3} \xrightarrow[1600\ K]{\text{Heat}} \underset{\text{Lime}}{CaO} + CO_2$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

Structure of CO_2 molecule

In CO_2 molecule, carbon undergoes *sp* hybridisation. Two *sp* hybridised orbitals of carbon atom overlap with two *p*-orbitals of oxygen atoms to form two sigma bonds while other two electrons of carbon atom are involved in $p\pi$—$p\pi$ bonding with oxygen atoms. This results in linear shape of carbon dioxide molecule. The C—O bonds in CO_2 molecule are of equal length (115 pm) and the molecule has zero dipole moment. This is explained on the basis of resonance structures as :

$$:\ddot{O}=C=\ddot{O}: \longleftrightarrow :\ddot{\underset{\cdot\cdot}{O}}^{-}—C\equiv\overset{+}{O}: \longleftrightarrow :\ddot{\underset{\cdot\cdot}{O}}^{+}\equiv C—\ddot{\underset{\cdot\cdot}{O}}:^{-}$$

Due to resonance, the C—O bond length is between double bond (122 pm) and triple bond (110 pm).

Properties

Carbon dioxide has different physical characteristics than carbon monoxide. Some important physical properties of CO and CO_2 are given in Table 7.

Table 7. Some physical properties of CO and CO_2.

Property	CO	CO_2
Melting point (K)	68	216.4 (at 5.2atm)
Boiling point (K)	81.5	194.5 (sublimes)
Density (g cm^{-3} at 273 K)	1.250	1.977
C—O bond length (pm)	112	115
Heat of formation (kJ mol^{-1})	110.5	–393.5

1. It is a colourless, odourless gas about 1.5 times heavier than air with density of 1.977 g L^{-1} at 298 K.

2. Unlike CO, it is not poisonous but it does not support life in animals and human beings. Animals and human beings die in it for lack of oxygen.

3. Solubility. Carbon dioxide is slightly soluble in water. Its solubility in water, however, increases with increase in pressure. Soda water and other aerated soft drinks are solutions of carbon dioxide in water (containing sugar, some flavouring and colouring substances) under pressure.

4. Carbon dioxide can be readily liquefied under a pressure of 50–60 atm. at room temperature. When liquid carbon dioxide is allowed to evaporate rapidly, it changes to a solid called solid carbon dioxide.

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The solid carbon dioxide is also called **dry ice** because it looks like ice. However, unlike ordinary ice, it does not wet a piece of cloth because it sublimes (changes to vapours without melting). It is a soft, snow like substance. It is used as refrigerant for ice-cream and frozen food. Mixed with ether or acetone, it forms freezing mixture with very low temperature and is used as a coolant for preserving perishable foodstuffs.

A mixture of solid CO_2 and ether can generate a low temperature of about –108°C, which is used in the liquefication of other gases.

5. Non-combustible nature. Ordinary carbon dioxide is neither combustible nor supporter of combustion. Therefore, it is used in fire extinguishing. However, certain active metals such as Na, K, Mg, etc. continue burning in it.

$$2Mg + CO_2 \longrightarrow 2MgO + C$$

6. Acidic nature. Carbon dioxide turns blue litmus red and is therefore, acidic in nature. It dissolves in water forming carbonic acid (H_2CO_3).

$$CO_2 + H_2O \rightleftharpoons \underset{\text{Carbonic acid}}{H_2CO_3}$$

Therefore, carbon dioxide is regarded as an *anhydride of carbonic acid.*

Carbonic acid is a weak dibasic acid and forms two series of salts namely *bicarbonates* (hydrogen carbonates) containing the HCO_3^- anion, and the *carbonates*, containing CO_3^{2-} anion.

$$H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) \longrightarrow H^+(aq) + CO_3^{2-}(aq)$$

Thus, a solution of carbon dioxide in water is an equilibrium mixture of CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}. It may be noted that these equilibria play an important role in carbonic acid-hydrogen carbonate ion buffer system in maintaining the *p*H of human blood between 7.26 to 7.42. Furthermore, the rate at which CO_2 comes in equilibrium with H_2CO_3 is slow and has significant role in the physiology of CO_2.

7. Action with lime water. On passing carbon dioxide gas through lime water, milkiness is produced due to the formation of calcium carbonate.

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{Milky}}{CaCO_3} + H_2O$$

However, on passing excess of CO_2 gas through the milky solution, the milkiness disappears due to the formation of calcium bicarbonate which is soluble.

$$CaCO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Milkiness disappears}}{Ca(HCO_3)_2}$$

8. Photosynthesis. Carbon dioxide, which is normally present to the extent of about 0.03% by volume in the atomosphere, is removed from it by the process known as **photosynthesis.** It *is the process by which the green plants convert atmospheric CO_2 into carbohydrates such as glucose.* Carbon dioxide is absorbed by plants in the presence of *chlorophyll* (green colouring matter in the leaves) and sunlight to form glucose, starch and cellulose (which are known as carbohydrates).

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

$$6nCO_2 + 5nH_2O \longrightarrow \underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + 6nO_2$$

By the process of photosynthesis, the plants prepare food for themselves as well as for animals and human beings. But the increased use of fossil fuels for combustion and decomposition of limestone for cement manufacture in recent years has considerably increased the CO_2 content in the atmosphere. This may lead to increase in greenhouse effect and thus raise the temperature of atmosphere which might result in serious consequences.

9. Action of ammonia. When CO_2 is reacted with liquid ammonia at 453–473 K under a pressure of 220 atmospheres, it first forms ammonium carbamate which decomposes to give urea.

$$2NH_3 + CO_2 \xrightarrow[220\text{ atm}]{453-473\text{ K}} \underset{\text{Ammonium carbamate}}{NH_2COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2} + H_2O$$

Uses of carbon dioxide. Carbon dioxide is used :

(*i*) in the preparation of aerated waters like soda water.

(*ii*) as a fire extinguisher because it is a non-supporter of combustion.

(*iii*) in the manufacture of washing soda by Solvay's process.

(*iv*) as a refrigerant in the form of solid carbon dioxide **(dry ice).** Solid carbon dioxide can sublime to the gaseous state without passing through the liquid state and therefore, it is called dry ice. It is also used as coolant for preserving perishable food items such as meat. Dry ice is also used for curing local burns and in hospitals for surgical operations of sores.

(*v*) carbon dioxide is also used in the manufacture of urea by reaction with ammonia.

$$CO_2 + 2NH_3 \longrightarrow \underset{\substack{\text{Ammonium}\\\text{carbamate}}}{NH_2COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

(*vi*) for artificial respiration (for the victims of carbon monoxide poisoning) as a mixture of 95% oxygen and 5% carbon dioxide (called ***carbogen***).

(*vii*) for the purification of cane sugar juice in the manufacture of sugar.

(*viii*) in plants during photosynthesis of glucose, starch and cellulose.

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LEARNING PLUS

We know that a gaseous substance can be liquefied by applying pressure only if it is below its critical temperature. For CO_2, the critical pressure is $73 \times 1.013 \times 10^5$ Pa and critical temperature is 304 K. A substance above its critical pressure is called a *supercritical fluid*.Though it is a gas, it is very dense and, therefore, can behave as a solvent.

In recent years carbon dioxide above its critical pressure known as **super-critical** CO_2 is used as a solvent to extract organic compounds from their natural sources (*e.g.,* caffeine from coffee beans, perfumes from plants or flowers) or to carry out industrial important reactions.

(2) Silicon dioxide

Silicon dioxide is also called **silica.** Most of the earth's crust (95%) is made up of silica and silicates. Silica occurs in several crystallographic forms such as **quartz**, **cristobalite** and **tridymite**. Each of these has different structures at high and low temperatures and they are inter convertible at suitable temperature. Among these α-quartz is the most common form and the major constituent of many rocks such as granite and sand stone. Pure SiO_2 is colourless but traces of other metals may colour it giving semi-precious gem stones such as **amethyst** (violet), **citrine** (yellow), **rose quartz** (pink), **smoky quartz** (brown) and non-precious materials such as **flint** (often black due to C), **agate** and onyx.

Silicon dioxide is a covalent, three dimensional network solid. In this structure (Fig. 12), each silicon atom is tetrahedrally surrounded by four oxygen atoms. Each oxygen atom in turn is covalently bonded to another silicon atoms as shown in the diagram. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms. Thus, there are no discrete SiO_2 units and it is a network solid.

GeO_2, SnO_2 and PbO_2 are all network solids.

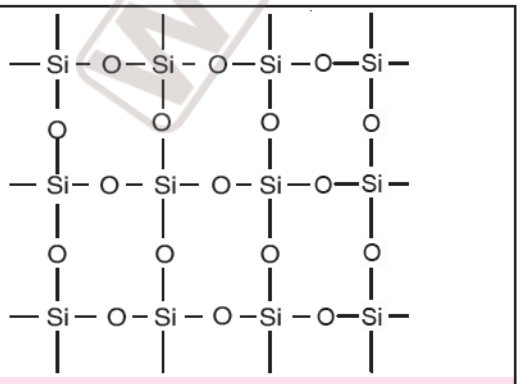

Fig. 12 Structure of SiO_2

Explanation. Carbon atom has a small size and forms stable multiple covalent bonds because of close interaction between the 2*p*–orbitals on carbon and 2*p*–orbitals on oxygen. This is because the energy of 2*p*–orbitals of carbon and 2*p*–orbitals of oxygen are nearly the same and they can easily overlap. However, silicon has large size and the 3*p*–orbitals of Si do not overlap effectively with 2*p*–orbitals of oxygen. Therefore, Si=O bonds are not formed. The tetravalency of silicon is satisfied by the formation of O – Si – O bonds which result in a network structure.

Silica in its normal forms is almost non-reactive because of very strong Si—O bond (bond enthalpy = 368 kJ mol^{-1}). Therefore, it has very high melting point and resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures.

However, silica is attacked by F_2, HF and NaOH.

$$SiO_2 + 2F_2 \longrightarrow \underset{\text{Silicon tetrafluoride}}{SiF_4} + O_2$$

$$SiO_2 + 4HF \longrightarrow \underset{\text{Silicon tetrafluoride}}{SiF_4} + 2H_2O$$

$$SiO_2 + 2NaOH \xrightarrow{\text{Fuse}} \underset{\text{Sodium silicate}}{Na_2SiO_3} + 2H_2O$$

Uses of Silica

The different forms of silica have many uses. The most important application of **quartz** is as a *piezoelectric material* and is used in crystal oscillators for radios and computers, filters for frequency control and in electro-metallurgical devices such as **transducers** and pick ups. The silica has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications.The coloured varieties of quartz are used as gemstones e.g., amethyst, jespar, opal, etc.

Vitreous silica has a low coefficient of expansion, quite resistant to shock and is quite transparent to visible and ultraviolet light. Therefore, it is used for laboratory glassware and for optical components such as lenses and prisms and cells for samples in UV-visible spectrophotometers.

Silica gel is amorphous and very porous. It is widely used as a drying agent, a catalyst and in chromatography. The mineral opal, which is used as a white or pearl like gemstone is hard (amorphous) silica gel.

Kieselguhr is another form of SiO_2 and is a fine powder. It is used in filtration plants as an abrasive and an inert filter.

Silica is also used in making refractory bricks for furnace lining sand (finely ground) and is used in the extraction of phosphorus from phosphates.

SILICONES

Silicones are organosilicon polymeric compounds containing Si—O—Si linkages. These have the general formula $(R_2SiO)_n$ having $(R_2SiO\rightarrow$ as a repeating unit.

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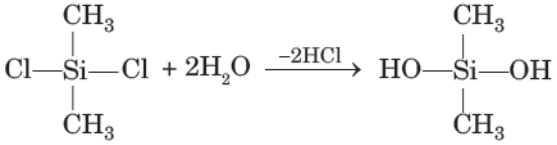
These may be linear, cyclic or cross linked. These have very high thermal stability and are called *high temperature polymers* (R may be alkyl or phenyl group). The starting material for the manufacture of silicones is alkyl or aryl substituted chlorosilanes.

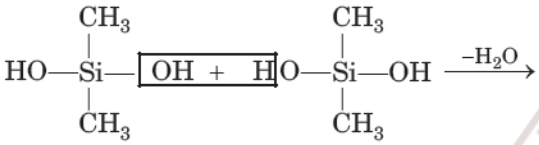
For example, when methyl chloride reacts with silicon in the presence of copper as catalyst at a temperature 573 K, various types of methyl substituted chlorosilanes of the formula CH_3SiCl_3 (or $MeSiCl_3$), $(CH_3)_2SiCl_2$ (or Me_2SiCl_2), $(CH_3)_3SiCl$ (or Me_3SiCl) alongwith small amount of $(CH_3)_4$ Si (or Me_4Si) are formed. Hydrolysis of dimethyl dichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation yields straight chain polymers.

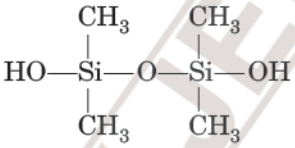
$$2CH_3Cl + Si \xrightarrow[573\ K]{Cu\ powder} (CH_3)_2SiCl_2$$

Dimethyl dichlorosilane



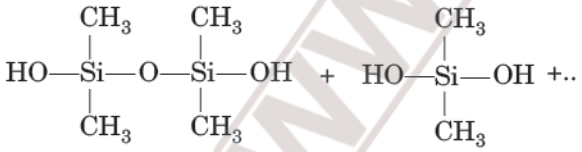
When two molecules of dimethylsilinol combine, we get dimer with the elimination of a molecule of water.

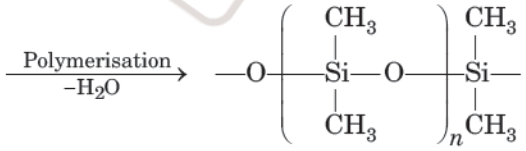




Dimer

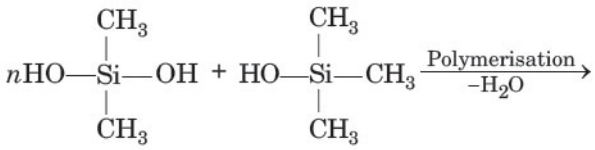
Since an active —OH group is left on each end of the chain, polymerisation reaction continues and the length of the chain increases forming linear silicone as

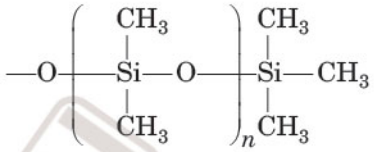




Silicone

The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends as shown in the reaction :

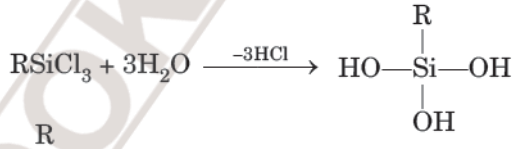


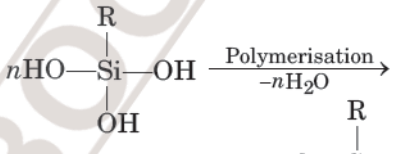


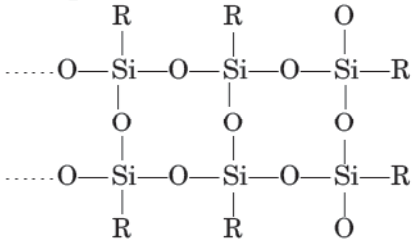
Silicone

The hydrolysis of monotrichloro silanes, $RSiCl_3$ gives cross linked polymers. By regulating the conditions, the condensation can be stopped at any stage and the chains or rings of desired lengths can be obtained.

$$RCl + Si + 2HCl \xrightarrow{Cu,\ 573K} R\ SiCl_3 + H_2$$







Cross linked silicone

The commercial silicone polymers are usually methyl derivatives and to lesser extent phenyl derivatives.

Properties of silicone polymers

1. Silicone polymers are highly stable towards heat. They have generally high thermal stability.

2. They have high dielectric strength.

3. Low molecular weight silicon polymers are soluble in organic solvents like ether, carbon tetrachloride, benzene, etc.

4. They are stable towards chemical reagents. They are not affected by weak acids, alkalies and salt solutions and are resistant to oxidation.

5. They are water repellants because they are surrounded by non-polar alkyl groups..

6. They are good electrical insulators.

7. They are resistant to oxidation. However, when heated in air to 350 to 400°C, silicones are rapidly oxidized and this leads to cross linking.

Uses of silicone polymers. The important uses of silicone polymers are :

(*i*) Silicone polymers are used for high temperature oil baths, high vacuum pumps etc.

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(*ii*) Silicone polymers are used as sealant, greases, varnishes and these can be used even at very low temperatures (of the order of –40°C).

(*iii*) Because silicones are water repellants and good insulators, they are used for water proofing of fabrics and in electrical condensers.

(*iv*) These are used as lubricants at both high and low temperatures.

(*v*) Silicone rubbers are very useful because they retain their elasticity at lower temperatures as compared to other rubbers. They are also mixed in paints to make them damp resistant.

(*vi*) They are used as excellent insulators for electric motors and other electrical appliances.

(*vii*) Being biocompatible, they are also used in surgical and cosmetic plants.

GLASS

Glass *is an amorphous and transparent or translucent solid obtained by solidification of a mixture of silicates of different metals, one of which is always an alkyl metal.* Ordinary glass is a mixture of sodium and calcium silicates and is obtained by heating a mixture of sand (SiO_2) with sodium carbonate and calcium oxide in a furnace at around 1700 K and then rapidly cooling.

$$CaO + Na_2CO_3 + SiO_2 \xrightarrow{1700\ K} \underbrace{Na_2SiO_3.CaSiO_3.4SiO_2}_{\text{Glass}} + CO_2$$

This type of glass is called **soda lime glass** or **soft glass.** It has an approximate composition : $Na_2SiO_3.CaSiO_3.4SiO_2$ or $Na_2O.CaO.6SiO_2$.

- Addition of small amounts of transition metal salts to the glass mixture impart colour to glasses. For example, addition of Cr(III) compounds imparts green colour, addition of Mn(IV) compounds imparts violet colour, addition of Co(II) salts imparts blue colour, addition of Fe(III) salts imparts brown colour and so on.

Some other varieties of glass are :

- **Lead potash glass or flint glass** is obtained by addition of lead oxide and potassium carbonate which has a high refractive index. It is used for making cut glass objects and lenses for optical purposes.
- **Borosilicate glass** is obtained by addition of boric oxide or borax to replace part of SiO_2. It is heat resistant glass with a low coefficient of thermal expansion. This type of glass is called **pyrex glass, corning** or **borosil** (trade names), and can withstand sudden changes in temperature and is used for making laboratory glassware.
- **Crook's glass** contains cesium oxide (CeO_2) and has the properties to cut off ultraviolet rays which are harmful to eyes. It is used in making lenses.

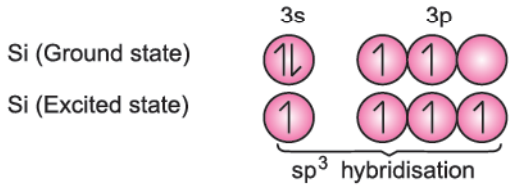
It may be noted that glass is not a true solid and has no definite melting point. It softens on heating to a certain temperature. It is vitreous amorphous material. Although glass is made up of SiO_4^{4-} tetrahedral units, these are not arranged in any definite or regular pattern as in crystalline silicates or in quartz. Thus, glass behaves more or less like a fluid. Moreover, since glass is obtained when molten silicates are allowed to cool rapidly, therefore, glass is regarded as a **super cooled liquid.**

SILICATES

The silicates are the compounds of silicon and oxygen. A large number of silicate minerals exist in nature. Some of these important minerals are : **feldspars** *e.g., albite*, $NaAlSi_3O_8$, **zeolites** *e.g., chabazite,* $Ca_2[(AlO_2)_4(SiO_2)_8.H_2O]$, **micas** (*muscovite*), $[KAl_2(Si_3AlO_{10})(OH)_2]$ and **asbestos** $[Mg_3(Si_2O_5)(OH)_4]$. Silicates occur in the earth's crust in the form of numerous silicate minerals and alumino-silicate clays.

All silicates involve silicon-oxygen single bonds. These are of two types. Terminal –Si–O bonds involving oxygen bonded to silicon and no other atoms and bridging –Si–O–Si bonds involving oxygen bonded to two silicon atoms. **The basic building unit of all silicates is the tetrahedral SiO_4^{4-} ion.**

In SiO_4^{4-} tetrahedral, the four oxygen ions are arranged at the four corners of the tetrahedron with silicon atoms at the centre. This can also be predicated from hybridisation. In this ion, silicon involves sp^3 hybridisation. The outer electronic configuration of silicon atom in ground state is $3s^2 3p^2$. To account for tetravalency, one of the electron from 3*s*-orbital is promoted to vacant 3*p*-orbital and its electronic configuration in excited state becomes : $3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1$. These orbitals get hybridised forming four sp^3 hybrid orbitals. They form four bonds with oxygen atoms giving SiO_4 unit. Each oxygen atom gets one



electron each form some metal in order to complete its octet resulting SiO_4^{4-} anion. Since, it involves sp^3

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hybridisation, it has tetrahedral structure, as given in Fig. 13.

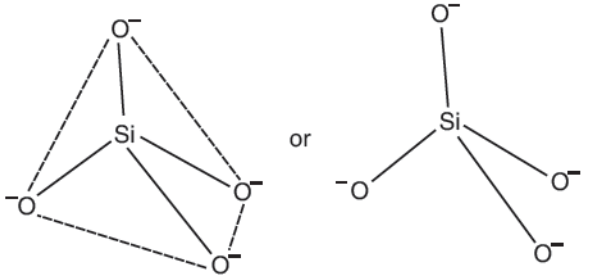

Fig. 13. Tetrahedral structure of SiO_4^{4-} anion.

For simplicity, the SiO_4^{4-} unit is represented as shown in Fig. 14, in which the plane circles represent oxygen atoms and small solid circle represents silicon atom.

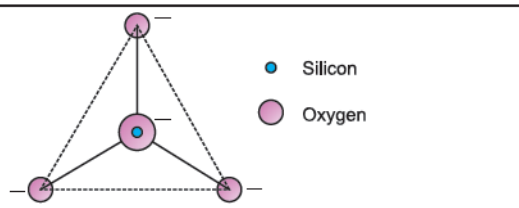

Fig. 14. Representation of SiO_4^{4-} units.

Types of silicates

In silicates, either the discrete unit is present or a number of such units are joined together by sharing 1, 2, 3 or 4 oxygen atoms per silicate unit. When these silicate units are linked together, they form **chain, ring, sheet** or **three dimensional structures.** The negative charge on silicate structure is neutralised by positively charged metal ions. Depending upon the linkages of SiO_4^{4-} tetrahedral units, the silicates may be classified into the following types :

1. Ortho silicates. These are simple silicates which contain discrete SiO_4^{4-} units as shown in Fig. 13.

The common examples of ortho-silicates are : *Zircon* ($ZrSiO_4$), *Wellimite* (Zn_2SiO_4), *Phenacite* (Be_2SiO_4).

2. Pyrosilicates or islands. When two SiO_4^{4-} tetrahedral share a corner (common oxygen), island structures are obtained. These contain discrete $[Si_2O_7]^{6-}$ units as shown in Fig. 15. Since this anion carries six negative charges, the number of cations is such that they balance the negative charge. The common examples are :

Thortveitite ($Sc_2Si_2O_7$),

hemimorphite $[Zn_4(OH)_2Si_2O_7]$

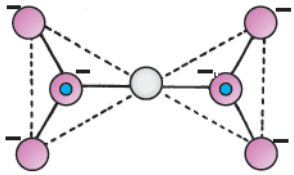

Fig. 15. Structure of $[Si_2O_7]^{6-}$ unit in island or pyrosilicates

3. Cyclic silicates. When two oxygens of each SiO_4^{4-} tetrahedron are shared with others, cyclic or ring structures are obtained as shown in Fig. 15. The primary unit in these silicates is $(SiO_3)^{2-}$. There are two types of cyclic ions : $[Si_3O_9]^{6-}$ as shown in Fig. 16 (*a*) and cyclic ion $[Si_6O_{18}]^{12-}$ as shown in Fig. 16(*b*).

$[Si_3O_9]^{6-}$ ion occurs in *wollastonite* $[Ca_3Si_3O_9]$ and cyclic $[Si_6O_{18}]^{12-}$ ions occurs in *beryl* ($Be_3Al_2Si_6O_{18}$).

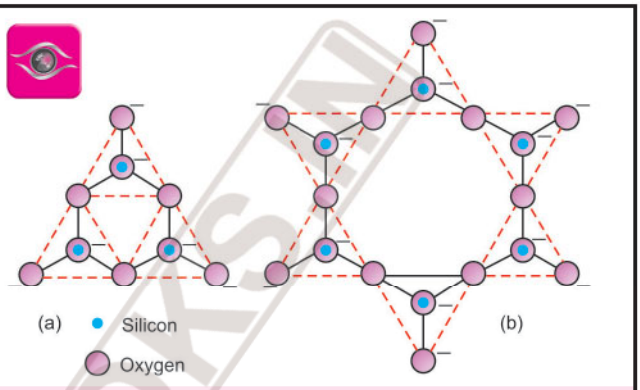

Fig. 16. Structure of cyclic silicates (*a*) $[Si_3O_9]^{6-}$ unit and (*b*) $[Si_6O_{18}]^{12-}$ unit.

4. Chain silicates. These are also formed by the sharing of two oxygen atoms of each SiO_4^{4-} units. There are two types of chain silicates : *single chain* and *double chain silicates.* Single chain silicates contain $(SiO_3)_n^{2-}$ chain and is shown in Fig. 17. The common examples of single chains are *pyroxenes* such as *diopside* $[CaMg(SiO_3)_2]$, *enstatite* ($MgSiO_3$), *spodumene* $[LiAl(SiO_3)_2]$.

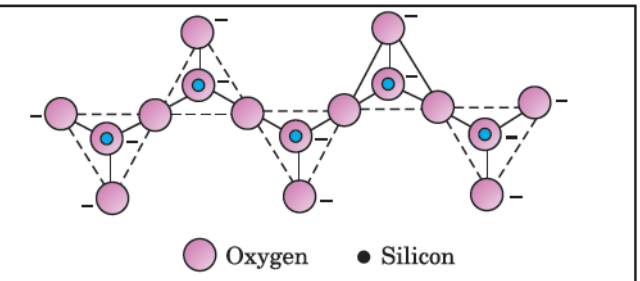

Fig. 17. Single chain silicates.

The double chain silicates contain $(Si_4O_{11})_n^{6-}$ are called *amphiboles.* The common examples of double chain silicates are :

Tremolite, $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$, *asbestos,* $CaMg_3O(Si_4O_{11})$.

5. Sheet silicates. These are formed by sharing of three oxygen atoms of each SiO_4^{4-} unit. The sharing gives an infinite two dimensional sheets and contain $(Si_2O_5)^{2-}$ type anions. Sheet silicates are shown in Fig. 18. The common examples are *kaolinite* $[Al(OH)_4Si_2O_5]$, *talc* $Mg_3(OH)_3Si_4O_{10}$. Clay also belongs to this type of family containing $(Si_2O_5)^{2-}$ anion.

6. Three-dimensional silicates. When all the four oxygens of SiO_4^{4-} units are shared, a three-dimensional network is obtained. Since all the oxygens are shared the silicate is neutral. The common examples are different forms of silica such as *quartz,*

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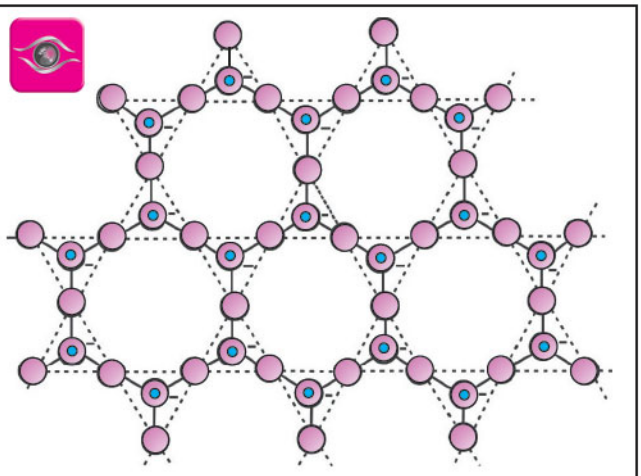


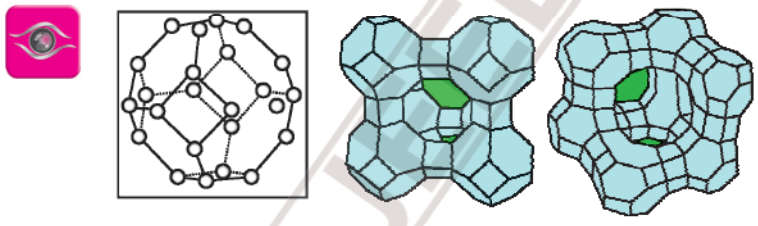
Fig. 18. Sheet silicates

tridymite and *cristobalite*. These have the general formula $(SiO_2)_n$.

In some cases, Si^{4+} is replaced by Al^{3+} in tetrahedral positions in SiO_3 lattice. In such cases, the presence of an additional monovalent cation is necessary to maintain electrical neutrality. For example, *feldspar* ($KAlSi_3O_8$), *zeolites* ($NaAlSi_2O_6.H_2O$).

ZEOLITES

Zeolites are microporous aluminosilicates having the general formula $M_{x/n}[AlO_2]_x[SiO_2].mH_2O$. In zeolites, aluminium atoms replace few silicon atoms in three dimensional network of silicon dioxide. The overall structure known as alumino silicates acquires a negative charge. Cations such as Na^+, K^+ or Ca^{2+} balance the negatives charge.These have open structure of aluminosilicate frameworks which enables them to take up loosely bound water or other small molecules in their structures. The negative charge of the alumino silicate framework is neutralised by exchangable cations of valence *n*. Zeolites have high porosity due to the presence of one, two or three dimensional network of interconnected channels and cavities of molecular dimensions. These give them honey comb like structure. For example, Fig. 19(*a*) shows a single cavity from 24 linked $[SiO_4]$ tetrahedra. It is called the b-cage or sodalite cage. Fig. 19(*b*) shows the zeolite which is formed by linking sodalite cages through double four membered rings and Fig. 19(*c*) is formed by linking the sodalite cages through double six membered rings.



(*a*) (*b*) (*c*)

Fig. 19. Structure of zeolites

Uses of Zeolites

(*i*) Zeolites are used as molecular sieves and can separate molecules of different sizes.

(*ii*) These are extensively used as catalysts in petrochemical inderstries for working of hydrocarbons and isomerization. For example. ZSM– 5 (a type of zeolite) is used to convert alcohols directly in to gasoline.

(*iii*) Hydrated zeolites are also used as ion-exchange materials in softening of hard water.

SOLVED EXAMPLES

❑ Example 16.

Carbonic acid is a weak dibasic acid and solutions of carbonates or hydrogen carbonates are alkaline. Write balanced equations for the hydrolysis of HCO_3^- and CO_3^{2-} ions

Solution:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

❑ Example 17.

What is the oxidation state of carbon in each of the following :

(i) CO_2 *(ii)* CO *(iii)* CaC_2 *(iv)* H_2CO_3 *(v)* HCN.

Solution:

(*i*)	CO_2	:	+4
(*ii*)	CO	:	+2
(*iii*)	CaC_2	:	+1
(*iv*)	H_2CO_3	:	+4
(*v*)	HCN	:	+2

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❑ Example 18.

What is the state of hybridization of carbon in (i) diamond and (ii) graphite (iii) carbonate ion

Solution: (*i*) Diamond : sp^3

(*ii*) Graphite : sp^2

(*iii*) CO_3^{2-} ion : sp^2

❑ Example 19.

Select the members of group 14 which

(i) forms the most acidic dioxide.

(ii) is commonly found in +2 oxidation state

(iii) used as semiconductor

Solution:

(*i*) Carbon (*ii*) Lead (*iii*) Silicon and germanium

❑ Example 20.

Explain the following reactions :

(i) Silicon is heated with methyl chloride at high temperature in the presence of copper.

(ii) Silicon dioxide is treated with hydrogen fluoride.

(iii) CO is heated with ZnO.

(iv) Hydrated alumina is treated with aqueous NaOH.

Solution: (*i*) Dichlorodimethyl silicon is formed

$$2CH_3Cl + Si \xrightarrow[570\,K]{Cu\ powder} (CH_3)_2SiCl_2$$

(*ii*) Silicon tetrafluoride is formed which dissolves in HF to form hydrofluoro silicic acid.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \longrightarrow \underset{\text{Hydrofluoro silicic acid}}{H_2SiF_6}$$

(*iii*) ZnO is reduced to zinc.

$$ZnO + CO \longrightarrow Zn + CO_2$$

(*iv*) Alumina dissolves to form sodium meta-aluminate.

$$\underset{\text{Hydrated alumina}}{Al_2O_3.2H_2O} + 2NaOH(aq) \xrightarrow{Heat} \underset{\text{Sodium meta-aluminate}}{2NaAlO_2} + 3H_2O$$

or $Al_2O_3.2H_2O(l) + 2NaOH(aq) + H_2O(l) \xrightarrow{Heat} \underset{\text{Sodium tetrahydroxoaluminate (III)}}{2Na[Al(OH)_4](aq)}$

❑ Example 21.

Write balanced chemical equations for the following reactions :

(i) Combustion of C_4H_{10} in a limited supply of oxygen to form carbon monoxide and water.

(ii) The reaction of calcium carbide with water to form acetylene.

(iii) The preparation of calcium cyanamide from calcium carbide and nitrogen.

(iv) Formation of hydrogen cyanide from methane and ammonia.

Solution:

(*i*) $C_4H_{10}(g) + \frac{9}{2}O_2(g) \longrightarrow 4CO(g) + 5H_2O(l)$

(*ii*) $CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$

(*iii*) $CaC_2(s) + N_2(g) \longrightarrow CaNCN(s) + C(s)$

(*iv*) $CH_4(g) + NH_3 \xrightarrow[1500\,K]{Pt.\ Catalyst} HCN(g) + 3H_2(g)$

❑ Example 22.

A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is obtained. Monoxide of the element is a poweful reducing agent and reduces ferric oxide to iron. Identify the element and write formulas of its monoxide and dioxide. Write chemical equations for the formation of producer gas and reduction of ferric oxide with the monoxide.

(NCERT Exemplar Problem)

Solution: The tetravalent element is carbon which forms monoxide, CO and dioxide CO_2.

On passing air over heated element at 1273 K, producer gas CO, N_2 is obtained

$$2C(s) + \underbrace{O_2(g) + 4N_2(g)}_{\text{air}} \xrightarrow{1273\,K} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas}}$$

CO is a powerful reducing agent which reduces ferric oxide to iron.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

❑ Example 23.

Classify the following oxides as neutral, acidic, basic or amphoteric :

CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3

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Solution: CO : neutral B_2O_3 : acidic
SiO_2 : acidic CO_2 : acidic
Al_2O_3 : amphoteric PbO_2 : amphoteric
Tl_2O_3 : basic

❑ Example 24.

SiF_6^{2-} is known but $SiCl_6^{2-}$ is not known. Explain.

Solution: This is due to the following reasons :

(*a*) Silicon being small in size can accommodate 6 F atoms but cannot accommodate larger 6 Cl atoms.

(*b*) Due to smaller size of F, steric repulsions will be less in SiF_6^{2-}.

(*c*) Interaction of lone pair electrons of F with Si is stronger than that of Cl lone pairs.

❑ Example 25.

Although diamond is covalent, yet it has very high melting point. Explain.

Solution:

Diamond has three dimensional network structure involving strong carbon-carbon bonds. These bonds are difficult to break and therefore, the melting point of diamond is a very high.

❑ Example 26.

What are silicones ?

Solution:

Silicones are synthetic organosilicon compounds containing units held by Si—O—Si linkages.

The R groups may be alkyl or phenyl occupying the remaining positions on each silicon. They are hydrophobic *i.e.*, water repellent in nature.

Practice Problems

◑ **11.** Name two elements which exhibit allotropy.

◑ **12.** What is the composition of producer gas ?

◑ **13.** Which carbide is used for preparing acetylene ?

◑ **14.** Name the carbide called carborundum ?

◑ **15.** Which can be used as a lubricant—graphite or diamond ?

◑ **16.** Which oxide of carbon is an anhydride of carbonic acid ?

◑ **17.** Give the name of a compound used as a fire extinguisher under the name pyrene.

◑ **18.** Complete the following reactions :

(*i*) $HCOOH \xrightarrow[\text{Heat}]{H_2SO_4}$

(*ii*) $CO + H_2 \xrightarrow[200\text{ atm, }675\text{ K}]{ZnO,\ Cr_2O_3}$

(*iii*) $SiO_2 + C \longrightarrow$

(*iv*) $CaCO_3(aq) + CO_2$ (excess) $\longrightarrow$

◑ **19.** Among group 14 elements name

(*i*) the most electronegative element

(*ii*) most metallic element

(*iii*) the elements having highest tendency to form $p\pi$—$p\pi$ bonds.

◑ **20.** Predict the correct answer :

(*i*) more stable out of CH_4 and SiH_4

(*ii*) easily hydrolysed out of $SiCl_4$ and CCl_4

(*iii*) shows stable +2 oxidation state out of Sn and Pb.

◑ **21.** What is the product of

(*i*) hydrolysis of $SiCl_4$

(*ii*) reaction of SiF_4 and F^- ion

◑ **22.** What is the basic unit of all silicates ?

Answers to Practice Problems

◐ **11.** Carbon and phosphorus

◐ **12.** 2CO and $4N_2$

◐ **13.** Calcium carbide, CaC_2

◐ **14.** Silicon carbide, SiC

◐ **15.** Graphite

◐ **16.** CO_2

◐ **17.** Carbon tetrachloride

◐ **19.** (*i*) C (*ii*) Pb (*iii*) C.

◐ **20.** (*i*) CH_4 (*ii*) $SiCl_4$ (*iii*) Pb

◐ **21.** (*i*) Silicic acid $Si(OH)_4$
(*ii*) $[SiF_6]^{2-}$

◐ **22.** SiO_4^{4-}

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add on

Conceptual Questions 2

CONCEPTUAL QA

Q.1. $[SiF_6]^{2-}$ is known but $[CF_6]^{2-}$ is not formed. Explain.

Ans. Silicon has vacant *d*-orbitals and can form complex like $[SiF_6]^{2-}$ because Si can extend its coordination number beyond four. But $[CF_6]^{2-}$ is not formed because C has no vacant *d*-orbitals in its valence shell.

Q.2. $(CH_3)_3N$ is basic but $(CF_3)_3N$ is not basic. Explain.

Ans. This is due to different electronegativities of H and F bonded to nitrogen. In $(CH_3)_3N$, the lone pair on N is concentrated on N and so it can act as an electron pair donor (Lewis base). However, in $(CF_3)_3N$, the electron density on N is decreased due to strongly electronegative F atom attached to C. Hence, it cannot act as a Lewis base.

Q.3. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parenthness (give reactions only) :

(*i*) Silicon (*ii*) Linear silicon containing methyl groups only (*iii*) Na_2SiO_3 ***(I.I.T. 2001)***

Ans. (*i*) $3SiCl_4 + 4\,Al \longrightarrow 4AlCl_3 + 3Si$

(*ii*) $3SiCl_4 + 4Al \xrightarrow[\text{(molten)}]{} 4AlCl_3 + 3Si$

$Si + 2CH_3Cl \xrightarrow[570\ K]{Cu\ powder} (CH_3)_2SiCl_2$

$(CH_3)_2SiCl_2 \xrightarrow{HOH} HO{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{S}}}}{-}OH$

$n(CH_3)_2Si(OH)_2 \xrightarrow{Heat} -\left[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\right]_n$

Linear silicone

(*iii*) $SiCl_4 + 4H_2O \longrightarrow \underset{\text{Ortho silicic acid}}{H_4SiO_4} + 4HCl$

$H_4SiO_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$

$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + H_2O.$

Q.4. $SiCl_4$ forms $SiCl_6^{2-}$ while CCl_4 does not form CCl_6^{2-}. Explain.

Ans. Carbon does not have *d*-orbitals in its valence shell and therefore, cannot extend its octet. Hence CCl_4 cannot combine with Cl^- ions to form $[CCl_6]^{2-}$.

On the other hand, Si has vacant 3*d*-orbitals in its valence shell and can therefore, combine with Cl^- ions to forms $[SiCl_6]^{2-}$.

$$SiCl_4 + 2Cl^- \longrightarrow SiCl_6^{2-}.$$

Q.5. What is the maximum covalency of silicon in its compounds ?

Ans. Silicon shows maximum covalency in its compounds equal to six. For example, Na_2SiF_6.

Q.6. Account for the following :

(*i*) PbX_2 is more stable than PbX_4 (X = Cl, Br)

(*ii*) $PbCl_4$ is less stable than $SnCl_4$ but $PbCl_2$ is more stable than $SnCl_2$.

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Ans. (*i*) Due to inert pair effect, lead shows an oxidation state of +2. Hence, PbX_2 is more stable than PbX_4.

(*ii*) As we move down the group 14, the stability of +4 oxidation state decreases while that of +2 oxidation state increases due to inert pair effect. Therefore, lead shows stable +2 oxidation state ($PbCl_2$) while tin shows stable +4 oxidation state ($SnCl_4$).

CONCEPTUAL QA

Q.7. What is the importance of ultra pure elemental silicon ? How is it obtained ?

Ans. Ultra pure elemental silicon is used as a semiconductor. It is prepared by the reduction of highly pure silicon tetrachloride ($SiCl_4$) or silicon chloroform ($SiHCl_3$) with dihydrogen.

$$SiCl_4 + 2H_2(g) \xrightarrow{\text{Heat}} Si + 4HCl$$

$$SiHCl_3 + H_2 \longrightarrow Si + 3HCl$$

It can also be prepared by the pyrolysis of SiH_4,

$$SiH_4 \xrightarrow{\text{Heat}} Si + 2H_2$$

Q.8. Compare the behaviour of BCl_3 and CCl_4 with water.

Ans. BCl_3 readily gets hydrolysed with water to give boric acid.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 6HCl$$

CCl_4 does not get hydrolysed.

Q.9. What is dry ice ? Why is it so called ?

Ans. Solid carbon dioxide is called dry ice. Solid carbon dioxide can sublime to the gaseous state without passing through the liquid stage and, therefore, it is called dry ice.

Chapter Summary

Key Terms

- **Allotropes** are the different forms of the same element having different physical properties but almost similar chemical properties.
- **Silicones** are synthetic organosilicon polymers containing repeated R_2SiO units held by Si—O—Si bonds.
- **Silicates** are the compounds in which discrete SiO_4^{4-} tetrahedra units are present.
- **Zeolites.** These are microporous aluminosilicates having the general formula $M_{x/n}[AlO_2]_x[SiO_2].mH_2O$.

QUICK CHAPTER ROUND UP

GROUP 13 ELEMENTS

- **General electronic configuration:** ns^2np^1
- B, Al, Ga, In, Tl
- B and Al show an oxidation state of +3 while rest of the elements show two oxidation state of +3 and +1.
- On moving down the group, the stability of +3 oxidation state decreases while that of +1 oxidation state increases.
- Boron halides act as Lewis acids and Lewis acid strength decreases as $BI_3 > BBr_3 > BCl_3 > BF_3$
- On moving down the group, the acidic character of oxides and hydroxides changes gradually from acidic to amphoteric and their basic character increases.

B_2O_3	Al_2O_3, Ga_2O_3	In_2O_3	Tl_2O
$B(OH)_3$	$Al(OH)_3$, $Ga(OH)_3$	$In(OH)_3$	Tl(OH)
Acidic	Amphoteric	Basic	Strongly basic

- Borax is $Na_2B_4O_7.10H_2O$ or $Na_2[B_4O_5(OH)_4].8H_2O$. Its aqueous solution is alkaline due to hydrolysis.

On heating

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy Bead}}$$

- Boric acid (H_3BO_3) is a weak monobasic acid ($K_a = 1 \times 10^{-9}$). It behaves as a Lewis acid by accepting a pair of electrons from OH^-.
- H_3BO_3 contains triangular BO_3^{3-} ions in which boron is sp^2 hybridised.

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{373\ K} HBO_2 \xrightarrow{433\ K} H_2B_4O_7 \xrightarrow{\text{Red hot}} B_2O_3$$

- Diborane (B_2H_6) is electron deficient compound and has two three centred electron pair bonds.
- $B_3N_3H_6$ is called **inorganic benzene** or **borozole**.

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GROUP 14 ELEMENTS

- **General electronic configuration:** ns^2np^2
- C, Si, Ge, Sn, Pb
- Carbon and silicon show an oxidation state of +4. All other elements of this group show oxidation states of +2 and +4.
- The stability of +2 oxidation state increases on going down the group due to inert pair effect. Pb salts are more stable in +2 oxidation state than in +4 oxidation state.
- Due to small size and high electronegativity, carbon forms $p\pi$-$p\pi$ bonding.
- Carbon shows maximum catenation tendency which decreases as C >> Si > Ge ≈ Sn > Pb.
- Due to the absence of *d*-orbitals, carbon cannot extend its covalency beyond 4.
- CCl_4 cannot be hydrolysed while $SiCl_4$ can be easily hydrolysed because of absence of *d*-orbitals in carbon.
- In diamond, carbon undergoes sp^3 hybridisation and in graphite, carbon undergoes sp^2 hybridisation.
- Family of carbon allotropes consisting of cluster of carbon atoms such as C_{32}, C_{50}, C_{60}, C_{70}, C_{84}, etc. are called **fullerenes**.
- C_{60} is called Buckminster fullerene and is popularly known as **bucky ball**
- Silicon dioxide (called silica) has, three dimensional network solid in which each Si atom is bonded to four O atoms which are arranged tetrahedrally around it and each O atom is attached to two Si atoms by covalent bonds.

Silicates have SiO_4^{4-} basic structural units

- Orthosilicates SiO_4^{4-}
- Pyrosilicates $Si_2O_7^{6-}$
- Cyclic $(SiO_3)^{2-}$
- Chain silicates $(Si_4O_{11})_n^{6-}$
- Sheet silicates $(Si_2O_5)^{2-}$

- **Silicones** have repeated R_2SiO units held by Si–O–Si bonds.

NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. Discuss the pattern of variation in the oxidation states of (*i*) B to Tl and (*ii*) C to Pb.

Ans. (*i*) B shows only +3 oxidation state in it compounds whereas others also show +1 oxidation state. The +1 oxidation state becomes stable as Al < Ga < In < Tl. So, boron and Al show only +3 oxidation state, Ga and In can exhibit +3 and +1 oxidation states but +1 oxidation state of Tl is more stable than +3. The stability of lower oxidation state on moving down the group is due to inert pair effect.

(*ii*) The elements from C to Pb show +4 and +2 oxidation states. C and Si show mainly +4 oxidation states. Ge and Sn show +4 and +2 oxidation state but +4 is more stable than +2. However, for Pb, +2 oxidation state in more stable than +4. So the stability of +4 oxidation state decreases as Ge > Sn > Pb while the stability of +2 oxidation state increases as Ge < Sn < Pb due to inert pair effect.

For more detail *Refer Text Page 8,9 and 22.*

Q. 2. How can you explain higher stability of BCl_3 as compared to $TlCl_3$?

Ans. *Refer Conceptual Questions,* 1 *Q.9 Page 19.*

Q. 3. Why does boron triflouride behave as a Lewis acid ?

Ans. BF_3 has only six electrons around B in its valence shell and therefore, needs two more electrons to complete its octet. Therefore, it can readily accept a pair of electrons from Lewis bases such as F^-, $(C_2H_5)O$, etc and hence behave as a Lewis acid.

$$BF_3 + F^- \longrightarrow BF_4^-$$

Q. 4. Consider the compounds, BCl_3 and CCl_4. How will they behave with water ? Justify.

Ans. B atom in BCl_3 has only six electrons in the valence shell and therefore, is an electron deficient molecule. It can readily accept a pair of electrons donated by water and hence undergoes hydrolysis to form boric acid and HCl.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

In contrast, C atom in CCl_4 has 8 electrons in its valence shell. It does not have vacant *d*-orbitals to extend its octet. Therefore, it is an electron precise molecule and hence neither accepts nor donates a pair of electrons. Therefore, it does not accept a pair of electrons from H_2O molecule and hence CCl_4 does not undergo hydrolysis in water.

Q. 5. Is boric acid a protic acid ? Explain.

Ans. *Refer Conceptual Questions* 1 *, Q.8 (Page 19).*

Q. 6. Explain what happens when boric acid is heated.

Ans. *Refer Solved Example 3 (iii) (Page 17).*

Q. 7. Describe the shapes of BF_3 and BH_4^-. Assign the hybridisation of boron in these species.

Ans. In BF_3 , boron is sp^2 hybridised and therefore, it is a planar molecule. In $[BH_4]^-$, boron is sp^3 hybridised and therefore, it is a tetrahedral molecule.

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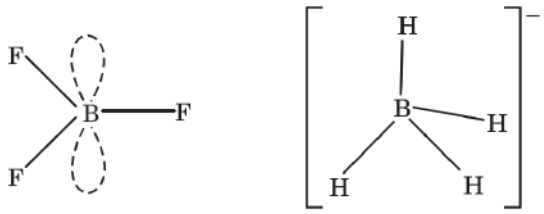


Q. 8. Write reactions to justify amphoteric nature of aluminium.

Ans. *Refer Conceptual Questions,* 1 *Q. 10 (Page 20).*

Q. 9. What are electron deficient compounds ? Are BCl_3 and $SiCl_4$ electron deficient species ? Explain.

Ans. (*i*) Electron deficient compounds are those in which the central atom either does not have eight electrons in the valence shell or it has eight electrons but can expand its valency beyond 4 due to the presence of vacant *d*-orbitals.

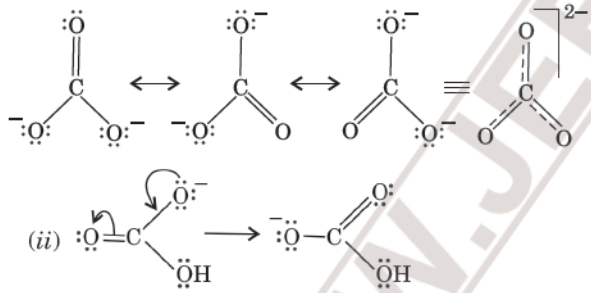
(*ii*) BCl_3 is an electron deficient species because it has 6 electrons in the valence shell of B atom. It accepts a pair of electrons from NH_3 to complete its octet.

$$Cl_3B + NH_3 \longrightarrow Cl_3B \longleftarrow NH_3$$

(*iii*) In $SiCl_4$, the central Si atom has 8 electrons but it can expand its valency beyond 4 due to the presence of vacant *d*-orbitals. Therefore, it may also be regarded as electron deficient.

Q. 10. Write the resonance structures of CO_3^{2-} and HCO_3^-.

Ans.



Q. 11. What is the state of hybridisation of carbon in (*a*) CO_3^{2-} (*b*) diamond (c) graphite ?

Ans. *Refer Solved Example 18 (Page 38).*

Q. 12. Explain the difference in properties of diamond and graphite on the basis of their structures.

Ans. *Refer Text page 26.*

Q. 13. Rationalise the given statements and give chemical reactions :

(*i*) Lead (II) chloride reacts with Cl_2 to give $PbCl_4$.

(*ii*) Lead (IV) chloride is highly unstable towards heat.

(*iii*) Lead is known not to form an iodide, PbI_4.

Ans. (*i*) Due to inert pair effect, Pb is more stable in +2 oxidation state than in +4 oxidation state. Therefore, lead (II) chloride is more stable than lead (IV) chloride and hence $PbCl_2$ does not react with Cl_2 to give $PbCl_4$.

(*ii*) Pb (+2) oxidation state is more stable than Pb (+4) because of inert pair effect. Therefore, Pb(IV)Cl_4 is unstable to heat and decomposes to give Pb(II)Cl_2.

$$PbCl_4 \xrightarrow{\text{Heat}} PbCl_2 + Cl_2$$

(*iii*) Due to strong oxidising power of Pb^{4+} and reducing power of I^- ion, PbI_4 does not exist.

Q. 14. Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.

Ans. *Refer Solved Example 15 (Page 18).*

Q. 15. If B—Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

Ans. *Refer Conceptual Questions* 1, *Q.13 (Page 20).*

Q. 16. Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

Ans. Anhydrous HF is a covalent compound and is strongly hydrogen bonded. Therefore, it does not give F^- ions and therefore, AlF_3 does not dissolve in HF. On the other hand, KF is an ionic compound and contains F^- ions. Therefore, it combines with AlF_3 to form the soluble complex as

$$AlF_3 + 3NaF \longrightarrow \underset{\substack{\text{Sod. hexafluoroaluminate}\\\text{(III) soluble complex}}}{Na_3[AlF_6]}$$

Because of smaller size and higher electronegativity B has much higher tendency to form complexes than Al. Therefore, when BF_3 is added to above solution, AlF_3 gets precipitated.

$$Na_3[AlF_6] + 3BF_3 \longrightarrow 3Na[BF_4] + AlF_3(s)$$

Sod. tetrafluoroborate (III) soluble complex

Q. 17. Suggest a reason as to why CO is poisonous.

Ans. CO is highly poisonous because of its ability to form a complex with haemoglobin in the red blood cells. Haemoglobin in the blood combines with oxygen and forms oxyhaemoglobin by a reversible reaction:

$$\text{Haemoglobin} + O_2 \rightleftharpoons \text{Oxyhaemoglobin}$$

Oxyhaemoglobin is formed in the lungs and is carried to the different cells where it gives its oxygen. However, CO forms bonds with haemoglobin more strongly than oxygen. Therefore, if CO is present, it will form stable compound with haemoglobin and this will destroy the oxygen carrying ability of the blood. As a result, blood will not take up oxygen easily, causing suffocation and finally death.

Q. 18. How is excessive content of CO_2 responsible for global warming ?

Ans. CO_2 is produced during combustion reactions. It is used by plants during photosynthesis and O_2 is released into the atmosphere. However, if the concentration of CO_2 in the atmosphere increases beyond a certain limit due to excessive combustion, some CO_2 will always remain unutilized. The excess CO_2 absorbs heat radiated by the earth. Some of it

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is dissipated into the atmosphere while the remaining part is redirected back towards earth's surface which heat up the atmosphere. As a result, temperature of the earth and other bodies on the earth increases. This is called green house effect. As a result of green house effect, global warming occurs which has serious consequences.

Q. 19. Explain structures of diborane and boric acid.

Ans. *Refer Text Fig. 6–8.*

Q. 20. What happens when

(*a*) Borax is heated strongly,

(*b*) Boric acid is added to water,

(*c*) Aluminium is treated with dilute NaOH,

(*d*) BF_3 is reacted with ammonia ?

Ans. (*a*), (*b*) *Refer Solved Example 4 (Page 17).*

(*c*) Dihydrogen is formed

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow 2Na^+[Al(OH)_4]^-(aq) + 3H_2(g)$$

(*d*) BF_3 being Lewis acid accepts a pair of electrons from NH_3 to form coordinate complex.

$$BF_3 + NH_3 \longrightarrow \underset{\text{Complex}}{BF_3.NH_3}$$

Q. 21. Explain the following reactions

(*a*) Silicon is heated with methyl chloride at high temperature in the presence of copper;

(*b*) Silicon dioxide is treated with hydrogen fluoride;

(*c*) CO is heated with ZnO;

(*d*) Hydrated alumina is treated with aqueous NaOH solution.

Ans. *Refer Solved Example 20 (Page 38).*

Q. 22. Give reasons :

(*i*) Conc. HNO_3 can be transported in aluminium container.

(*ii*) A mixture of dilute NaOH and aluminium pieces is used to open drain.

(*iii*) Graphite is used as lubricant.

(*iv*) Diamond is used as an abrasive.

(*v*) Aluminium alloys are used to make aircraft body.

(*vi*) Aluminium utensils should not be kept in water overnight.

(*vii*) Aluminium wire is used to make transmission cables.

Ans. (*i*) Aluminium reacts with conc. HNO_3 and becomes passive due to the formation of a very thin film of aluminium oxide on its surface which protects it from further action. Therefore, aluminium containers can be used to transport conc. HNO_3.

(*ii*) NaOH reacts with Al and evolve H_2 gas whose pressure can be used to open clogged drains.

$$2Al(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow 2NaAlO_2(aq) + 3H_2(g)$$

(*iii*) Graphite has layered structure in which different layers are held by weak van der Waals forces. Because of weak forces between layers, the layers can slip over one another. Hence graphite acts as a lubricant.

(*iv*) Diamond is very hard and therefore, it is used as an abrasive.

(*v*) Aluminium alloys such as duralumin is light, tough and resistant to corrosion and hence used to make aircraft body.

(*vi*) Al reacts with water and dissolved O_2 to form a thin layer of aluminium oxide.

$$2Al(s) + H_2O(l) + O_2(g) \longrightarrow Al_2O_3(s) + H_2$$

A very small amount of Al_2O_3 may dissolve to give very small amount (a few ppm) of Al^{3+} ions in the solution. Since Al^{3+} are injurious to health, therefore, drinking water should not be kept in aluminium utensils overnight.

(*vii*) On mass to mass basis, aluminium conducts almost twice as Cu. Therefore, it is used in transmission cables.

Q. 23. Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon.

Ans. Due to increase in atomic size and screening effect, the force of attraction of the nucleus for the valence electron decreases considerably in Si as compared to C. As a result, there is a phenomenal decrease in ionization enthalpy from C to Si.

Q. 24. How would you explain the lower atomic radius of Ga as compared to Al ?

Ans. On going from Al to Ga, there are 10 elements of the first transition series of *d*-block which have electrons in the inner *d*-orbitals. The *d*-orbitals screen the nucleus less effectively because of their shapes and poor penetration power. As a result, the effective nuclear charge in Ga becomes more than in Al and therefore, atomic radius becomes slightly less than Al.

Q. 25. What are allotropes ? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes ?

Ans. *Refer Text page 26.*

Q. 26. (*a*) Classify following oxides as neutral, acidic, basic or amphoteric :

CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3

(*b*) Write suitable chemical equations to show their nature.

Ans. (*a*) *Refer Solved Example 23 (Page 38).*

(*b*) *For chemical equations, pages 24–25.*

Q. 27. In some of the reactions thallium resembles aluminium, whereas in others it resembles with group I metals. Support this statement by giving some evidences.

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Ans. Thallium exhibits +3 and +1 oxidation states. Aluminium shows an oxidation state of +3. Like Al, thallium shows +3 oxidation state in some of its compounds such as Tl_2O_3, $TlCl_3$, etc. Like Al, Tl also forms octahedral complexes such as $[TlF_6]^{3-}$ like $[AlF_6]^{3-}$. Group I metals show oxidation state of +1. Like group I elements, Tl also shows +1 oxidation state (due to inert pair effect). It also forms compounds like TlCl, Tl_2O, $TlClO_4$, etc. like group I oxides, Tl_2O is strongly basic.

Q. 28. When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.

Ans. *Refer Solved Example Q.14 (Page 18).*

Q. 29. What do you understand by (*a*) inert pair effect (*b*) allotropy (*c*) catenation.

Ans. *Refer Text.*

Q. 30. A certain salt X, gives the following results :

(*i*) Its aqueous solution is alkaline to litmus.

(*ii*) It swells up to a glassy material Y on strong heating.

(*iii*) When conc. H_2SO_4 is added to a hot solution of X, white crystals of an acid Z separates out.

Write equations for all the above reactions and identify X, Y and Z.

Ans. *Refer Solved Example 7 (Page 17).*

Q. 31. Write balanced equations for :

(*i*) $BF_3 + LiH \longrightarrow$ **(*ii*)** $B_2H_6 + H_2O \longrightarrow$

(*iii*) $NaH + B_2H_6 \longrightarrow$ **(*iv*)** $H_3BO_3 \xrightarrow{\Delta}$

(*v*) $Al + NaOH \longrightarrow$ **(*vi*)** $B_2H_6 + NH_3 \longrightarrow$

Ans. *Refer Solved Example 3 (Page 17).*

Q. 32. Give one method for industrial preparation and one for laboratory preparation of CO and CO_2 each.

Ans. Carbon monoxide

(*i*) **Industrial.** by incomplete combustion of carbon:

$$2C(s) + O_2(g) \xrightarrow[\text{air}]{\text{Limited}} 2CO(g)$$

(*ii*) **Laboratory.** by dehydration of formic acid.

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow[373\ K]{H_2SO_4} CO + H_2O$$

Carbon dioxide

(*i*) **Industrial.** as a by-product on heating limestone.

$$CaCO_3(s) \xrightarrow[1600K]{\text{Heat}} CaO(s) + CO_2(g)$$

(*ii*) **Laboratory.** by action of dil HCl on $CaCO_3$,

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Q. 33. An aqueous solution of borax is

(*a*) neutral

(*b*) amphoteric

(*c*) basic

(*d*) acidic

Ans. (*c*)

Q. 34. Boric acid is polymeric due to

(*a*) its acidic nature

(*b*) the presence of hydrogen bonds

(*c*) its monobasic nature

(*d*) its geometry

Ans. (*b*) Boric acid is polymeric because of hydrogen bonding.

Q. 35. The type of hybridisation of boron in diborane is

(*a*) *sp* **(*b*) sp^2**

(*c*) sp^3 **(*d*) dsp^2**

Ans. (*c*)

Q. 36. Thermodynamically the most stable form of carbon is

(*a*) diamond **(*b*) graphite**

(*c*) fullerenes **(*d*) coal**

Ans. (*b*)

Q. 37. Elements of group 14

(*a*) exhibit oxidation state of +4 only

(*b*) exhibit oxidation state of +2 and +4

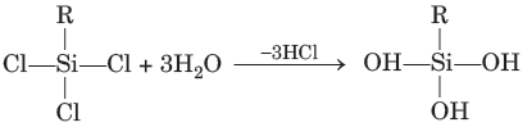
(*c*) form M^{2-} and M^{4+} ion

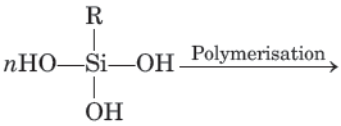
(*d*) form M^{2+} and M^{4+} ions

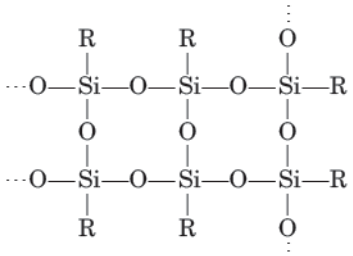
Ans. (*b*)

Q. 38. If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

Ans. Hydrolysis of $RSiCl_3$ gives cross linked silicones.







Cross linked silicone

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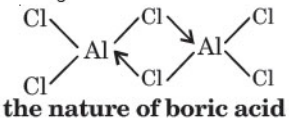
NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 61.*

Short Answer Questions *Carrying 2 or 3 marks*

Q. 1. Draw the structures of $BCl_3 \cdot NH_3$ and $AlCl_3$(dimer).

Ans. $BCl_3 \longleftarrow NH_3$



Q. 2. Explain the nature of boric acid as a Lewis acid in water.

Ans. Boric acid acts as Lewis acid in water by accepting a pair of electrons from hydroxyl ion :

$$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$$

Q. 3. Draw the structure of boric acid showing hydrogen bonding. Which species is present in water ? What is the hybridisation of boron in this species ?

Ans. *Refer Fig. 6 (Page 14)*
In water, boric acid is present as $[B(OH)_4]^-$.
Boron is sp^3 hybridised in it.

Q. 4. Explain why the following compounds behave as Lewis acids ?

(*i*) BCl_3 (*ii*) $AlCl_3$

Ans. BCl_3 and $AlCl_3$ are electron deficient molecules due to incomplete octets of central metal atoms and therefore, behave as Lewis acids.

Q. 5. Give reasons for the following :

(*i*) CCl_4 is immiscible in water, whereas $SiCl_4$ is easily hydrolysed.

(*ii*) Carbon has a strong tendency for catenation compared to silicon.

Ans. (*i*) *Refer Text, Page 24.*
(*ii*) *Refer Text, Page 25.*

Q. 6. Explain the following :

(*i*) CO_2 is a gas whereas SiO_2 is a solid.

(*ii*) Silicon forms SiF_6^{2-} ion whereas corresponding fluoro compound of carbon is not known.

Ans. (*i*) *Refer Text, Page 32–33.*
(*ii*) Silicon can extend the octet because of the persence of vacant *d*-orbitals but carbon cannot extend the octet.

Q. 7. The +1 oxidation state in group 13 and +2 oxidation state in group 14 becomes more and more stable with increasing atomic number. Explain.

Ans. Because of inert pair effect. *Refer Text (Page 6–7).*

Q. 8. Carbon and silicon both belong to the group 14, but inspite of the stoichiometric similarity, the dioxides, (*i.e.*, carbon dioxide and silicon dioxide), differ in their structures. Comment.

Ans. In CO_2, carbon is *sp* hybridised and it is a linear molecule. In SiO_2, Si is sp^3 hybridised and is tetrahedrally bonded to four O atoms. *Refer Text (Page 30–31).*

Subjective Questions

Q. 9. If a trivalent atom replaces a few silicon atoms in three dimensional network of silicon dioxide, what would be the type of charge on overall structure ?

Ans. If a few tetrahedral Si atoms in a three dimensional network structure of SiO_2 are replaced by an equal number of trivalent atoms, then one valency of each Si atom becomes free. As a result, each substitution of Si atom by a trivalent atom introduces one unit negative charge into three dimensional network structure of SiO_2. Hence, SiO_2 becomes negatively charged.

Q. 10. When BCl_3 is treated with water, it hydrolyses and forms $[B(OH)_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al(H_2O)_6]^{3+}$ ion. Explain what is the hybridisation of boron and aluminium in these species ?

Ans. Hybridisation of B in $[B(OH)_4]^-$ is sp^3.
Hybridisation of Al in $[Al(H_2O)_6]^{3+}$ is sp^3d^2.

Q. 11. Aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character. A piece of aluminium foil is treated with dilute hydrochloric acid or dilute sodium hydroxide solution in a test tube and on bringing a burning matchstick near the mouth of the test tube, a pop sound indicates the evolution of hydrogen gas. The same activity when performed with concentrated nitric acid, reaction doesnot proceed. Explain the reason.

Ans. Conc. HNO_3 makes aluminium passive by forming a protective layer of its oxide (Al_2O_3) on the surface of metal.

$$2Al + 6HNO_3 \longrightarrow Al_2O_3 + 6NO_2 + 3H_2O$$

This prevents further action.

Q. 12. Explain the following :

(*i*) Gallium has higher ionisation enthalpy than aluminium.

(*ii*) Boron does not exist as B^{3+} ion.

(*iii*) Aluminium forms $[AlF_6]^{3-}$ ion but boron does not form $[BF_6]^{3-}$ ion.

(*iv*) PbX_2 is more stable than PbX_4.

(*v*) Pb^{4+} acts as an oxidising agent but Sn^{2+} acts as a reducing agent.

(*vi*) Electron gain enthalpy of chlorine is more negative as compared to fluorine.

(*vii*) $Tl(NO_3)_3$ acts as an oxidising agent.

(*viii*) Carbon shows catenation property but lead does not.

(*ix*) BF_3 does not hydrolyse.

(*x*) Why does the element silicon not form a graphite like structure whereas carbon does.

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Ans. (*i*) Due to ineffective shielding of valence electrons by the intervening 3*d*-electrons, the effective nuclear charge on Ga is slightly higher than that on Al. Therefore, ΔH_i of Ga is slightly more than that of Al.

(*ii*) Because of small size of boron, sum of the first three ionization enthalpies is high and therefore, boron does not lose three electrons to form B^{3+} ions.

(*iii*) Al has vacant *d*-orbitals and hence can expand its coordination number from 4 to 6 and therefore, forms $[AlF_6]^{3-}$. But B does not have vacant *d*-orbitals and therefore, cannot expand octet. Hence it cannot form $[BF_6]^{3-}$.

(*iv*) *Refer Conceptual* Qs. 2, Q. 6(*i*) (*Page 40–41*).

(*v*) Lead shows stronger inert pair effect so that Pb^{2+} ion is more stable than Pb^{4+} ion whereas Sn^{4+} ion is more stable than Sn^{2+} ion. Therefore, Pb^{4+} are more readily reduced to Pb^{2+} as compared to Sn^{4+}. Thus, Pb^{4+} acts as a stronger oxidising agent.

(*vi*) Due to small size of fluorine, it has larger electron-electron repulsions. Therefore, electron gain enthalpy of F is less negative as compared to that of Cl.

(*vii*) Due to inert pair effect, Tl in +1 oxidation state is more stable than +3 oxidation state. Therefore, $Tl(NO_3)_3$ acts as an oxidising agent and gets reduced to stable +1 oxidation state.

(*viii*) *Refer Text (Page 23–24).*

(*ix*) BF_3 does not hydrolyse completely. Instead it undergoes incomplete hydrolysis to boric acid and fluoroboric acid because HF first formed reacts with H_3BO_3.

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF] \times 4$$
$$H_3BO_3 + HF \longrightarrow H^+ + [BF_4]^- + 3H_2O] \times 3$$
$$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3[BF_4]^- + 3H^+$$

(*x*) *Refer text (Page 25–26).*

Q. 13. Identify the compounds A, X and Z in the following reactions :

$$\mathbf{A + 2HCl + 5H_2O \longrightarrow 2NaCl + X}$$

$$\mathbf{X \xrightarrow[370K]{\Delta} HBO_2 \xrightarrow[>370K]{\Delta} Z}$$

Ans. $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + H_3BO_3$
Borax

$$H_3BO_3 \xrightarrow[370K]{\Delta} HBO_2 \xrightarrow[>370K]{\Delta} B_2O_3$$

A : $Na_2B_4O_7$; X : H_3BO_3 ; Z : B_2O_3

Q. 14. Complete the following chemical equations :

$$\mathbf{Z + 3LiAlH_4 \longrightarrow X + 3LiF + 3AlF_3}$$
$$\mathbf{X + 6H_2O \longrightarrow Y + 6H_2}$$
$$\mathbf{X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O}$$

Ans. $BF_3 + 3LiAlH_4 \longrightarrow B_2H_6 + 3LiF + 3AlF_3$
(Z) (X)

$B_2H_6 + 6H_2O \longrightarrow H_3BO_3 + 6H_2$
(X) (Y)

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$
(X)

Long Answer Questions *Carrying 5 marks*

Q. 15. Describe the general trends in the following properties of the elements in Groups 13 and 14.

(*i*) Atomic size

(*ii*) Ionisation enthalpy

(*iii*) Metallic character

(*iv*) Oxidation states

(*v*) Nature of halides

Ans. *Refer Text.*

Q. 16. Account for the following observations :

(*i*) $AlCl_3$ is a Lewis acid

(*ii*) Though fluorine is more electronegative than chlorine yet BF_3 is a weaker Lewis acid than BCl_3.

(*iii*) PbO_2 is a stronger oxidising agent than SnO_2.

(*iv*) The +1 oxidation state of thallium is more stable than its +3 state.

Ans. (*i*) $AlCl_3$ is an electron deficient compound and therefore, behaves as a Lewis acid.

(*ii*) BF_3 is a weaker Lewis acid than BCl_3 because of back bonding from filled 2*p*-orbital of fluorine to vacant orbital of B resulting $p\pi - p\pi$ back bond. *Refer Text Page 9.*

(*iii*) In PbO_2 and SnO_2, both lead and tin are present in +4 oxidation state. Due to inert pair effect, Pb^{2+} ion is more stable than Pb^{4+} ion and therefore, PbO_2 is readily reduced to PbO and therefore, PbO_2 is a stronger oxidising agent. On the other hand, Sn^{4+} is more stable than Sn^{2+} and therefore, Sn^{4+} ions are not readily reduced to Sn^{2+} ions and SnO_2 is not a stronger oxidising agent.

(*iv*) Due to inert pair effect, +1 oxidation state of thallium is more stable than +3. *Refer Text (Page 7).*

Q. 17. When aqueous solution of borax is acidified with hydrochloric acid, a white crystalline solid is formed which is soapy to touch. Is this solid acidic or basic in nature ? Explain.

Ans. When aqueous solution of borax is acidified with HCl, boric acid is formed which is a white crystalline solid.

$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$
Borax Boric acid

It acts as a Lewis acid.

Q. 18. Three pairs of compounds are given below. Identify that compound in each of the pairs which has group 13 element in more stable oxidation state. Give reason for your choice. State the nature of bonding also.

(*i*) $TlCl_3$, TlCl (*ii*) $AlCl_3$, AlCl

(*iii*) $InCl_3$, InCl

Ans. (*i*) TlCl is more stable and bonding is ionic.

(*ii*) $AlCl_3$ is more stable and bonding is covalent.

(*iii*) $InCl_3$ is more stable and bonding is covalent.

Q. 19. BCl_3 exists as monomer whereas $AlCl_3$ is dimerised through halogen bridging. Give reason. Explain the structure of the dimer of $AlCl_3$ also.

Ans. *Refer Text* (*Page 9–10*).

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Q. 20. Boron fluoride exists as BF_3 but boron hydride doesnot exist as BH_3. Give reason. In which form does it exist ? Explain its structure.

Ans. *Refer HOTS. Q. 1. Page 49.*

Q. 21.(*i*) What are silicones ? State the uses of silicones.

(*ii*) What are boranes ? Give chemical equation for the preparation of diborane.

Ans. *Refer Text.*

Q. 22. A compound (A) of boron reacts with NMe_3 to give an adduct (B) which on hydrolysis gives a compound (C) and hydrogen gas. Compound (C) is an acid. Identify the compounds A, B and C. Give the reactions involved.

Ans. Since compound (A) reacts with NMe_3 and forms an adduct (B), (A) must be a Lewis acid. Since the adduct (B) on hydrolysis gives an acid (C) and hydrogen gas, A must be B_2H_6 and (C) must be boric acid.

$$\underset{\text{Diborane (A)}}{B_2H_6} + 2NMe_3 \longrightarrow \underset{\text{Adduct (B)}}{2BH_3{\cdot}NMe_3}$$

$$BH_3{\cdot}NMe_3 + 3H_2O \longrightarrow \underset{\text{Boric acid (C)}}{H_3BO_3} + 6H_2 + NMe_3$$

Q. 23. A non metallic element of group 13, used in making bullet proof vests is extremely hard solid of black colour. It can exist in many allotropic forms and has unusually high melting point. Its trifluoride acts as Lewis acid towards ammonia. The element exhibits maximum covalency of four. Identify the element and write the reaction of its trifluoride with ammonia. Explain why does the trifluoride act as a Lewis acid.

Ans. The non-metallic element of group 13 is boron. It is an extremely hard substance and is used in making bullet proof vests. This shows maximum covalency of four.

$$H_3\ddot{N} + BF_3 \longrightarrow H_3N \rightarrow BF_3$$

Since B in BF_3 has only six electrons in its valence shell and needs two more electrons to complete the octet, it acts as a Lewis acid.

Q. 24. A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is obtained. Monoxide of the element is a powerful reducing agent and reduces ferric oxide to iron. Identify the element and write formulas of its monoxide and dioxide. Write chemical equations for the formation of producer gas and reduction of ferric oxide with the monoxide.

Ans. Producer gas is a mixture of CO and N_2. Therefore, the tetravalent element is carbon and its monoxide and dioxide are CO and CO_2 respectively.

$$2C(s) + \underbrace{O_2(g) + 4N_2(g)}_{\text{Air}} \xrightarrow{1273K} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas}}$$

The monoxide of carbon is a strong reducing agent and reduces ferric oxide to iron.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

QUICK MEMORY TEST

A. Say True or False

1. Carbon atoms in graphite are sp^2 hybridised while in diamond these are sp^3 hybridised.
2. BF_3 is a stronger Lewis acid than BCl_3.
3. PbO_2 is a stronger oxidising agent than SnO_2.
4. The first ionization enthalpy of gallium is lower than that of aluminium.
5. Orthosilicates contain two SiO_4^{4-} tetrahedra units.
6. Beryl is an example of pyrosilicates.
7. SiO_2 exists as three dimensional network solid.
8. Diborane structure has two three centre electron pair bonds.
9. B_2H_6 is also called inorganic benzene.
10. Boric acid is a protonic acid.
11. The stability of +4 oxidation state increases from C to Pb.
12. $[SiCl_6]^{2-}$ is known but $[SiF_6]^{2-}$ is not known.
13. PbI_4 is quite stable.
14. $TlClO_4$ is more stable than $Tl(ClO_4)_3$.
15. The aqueous solution of borax is alkaline.

B. Complete the missing links

1. Borate ion has ..... structure.
2. $SnCl_2$ acts as a ..... agent.
3. The basic building unit of silicates is .....
4. The most stable oxidation state of thallium is .....
5. Pyrosilicates contain ..... anion.
6. In $N(SiH_3)_3$, N atom is ..... hybridised.
7. The molecular formula of inorganic benzene is .....
8. ..... occurs as colemanite.
9. In group 14 elements, ... shows maximum inert pair effect.
10. In borax bead test, the bead consists of ..... and .....

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C. Choose the correct alternative

1. Graphite is thermodynamically *more / less* stable than diamond.
2. Reduction of $SiCl_4$ with dihydrogen gives *Si / SiH_4*.
3. +2 oxidation state of Pb is *more / less* stable than +4.
4. In diamond, C undergoes *sp^2 / sp^3* hybridisation.
5. Bond length of B—F in BF_3 is *less / more* than that in $[BF_4]^-$.
6. Carbon has *strong / weak* tendency for catenation than silicon.
7. The anhydride of carbonic acid is *CO_2 / CO*.
8. Strong heating of boric acid forms *metaboric acid / boron oxide*.
9. Dehydration of formic acid gives *CO / CO_2*.
10. Talc is an example of *sheet silicates / chain silicates*.

Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. **False :** BF_3 is a weaker Lewis acid than BCl_3.
3. True
4. False
5. **False :** Orthosilicates contain one SiO_4^{4-} tetrahedral unit.
6. **False :** It is an example of chain silicates.
7. True
8. True
9. False
10. False
11. False
12. **False :** $[SiF_6]^{2-}$ is known but $[SiCl_6]^{2-}$ is not known.
13. False
14. True
15. True.

B. Complete the missing links

1. trigonal planar
2. reducing
3. SiO_4^{4-} tetrahedra
4. +1
5. $Si_2O_7^{6-}$
6. sp^2
7. $B_3N_3H_6$
8. Boron
9. lead
10. Sodium metaborate, boric anhydride

Choose the correct alternative

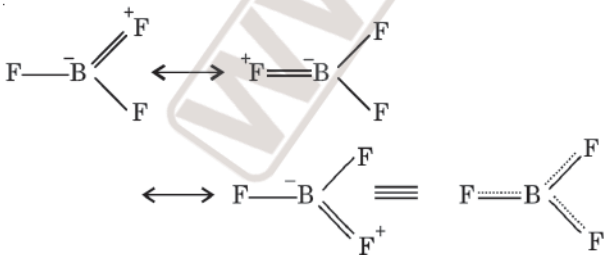
1. more
2. Si
3. more
4. sp^3
5. less
6. strong
7. CO_2
8. boron oxide
9. CO
10. sheet silicates

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q. 1. Explain why BF_3 exists but BH_3 does not.

Ans. In BF_3, the vacant $2p$-orbital of boron accepts π electron density by overlapping with filled $2p_z$ orbital of F. Therefore, the stability of BF_3 is due to back bonding.



However, hydrogen atoms do not have free electrons to form back bonding with boron and therefore, BH_3 is not stable. However, to satisfy the electron deficiency of boron, it dimerizes to form B_2H_6.

Q. 2. Gallium has higher ionization enthalpy than aluminium. Why ?

Ans. Gallium has higher ionisation enthalpy than aluminium because of higher effective nuclear charge. This is due to additional $3d^{10}$ electrons which do not shield the nuclear charge effectively so that the outer electrons are strongly held.

Q.3. Boron forms no compounds in unipositive state but thallium in unipositive state is quite stable. Why ?

Ans. Boron has electronic configuration $2s^2 2p^1$. It is always trivalent in its compounds. On the other hand, thallium prefers to form unipositive ions rather than tripositive ion. This is because of inert pair effect. In case of Tl ($[Xe]4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$), the outermost $6s^2$ electrons do not take part in bonding and behave like inert gas. Therefore, it forms stable Tl^+ compounds.

Q.4. Which of the following is not hydrolysed by water and why ?

BF_3, BCl_3 and BBr_3

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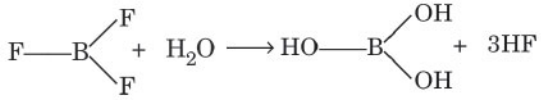
Ans. BF_3 is not easily hydrolysed by water. It forms an adduct $BF_3 . OH_2$ whereas BCl_3 and BBr_3 are hydrolysed to boric acid and HCl or HBr respectively.

This is because the B—F bond in BF_3 is very strong due to extensive $p\pi$—$p\pi$ back bonding. As a result, it is not hydrolysed by water. The B—F bond energy is far larger than B—OH bond energy and cannot be compensated.



(Not possible)

However, in BCl_3 and BBr_3, the corresponding B—Cl and B—Br bond energy is relatively less than B—F because of inefficient $p\pi$—$p\pi$ bonding. Therefore, these get hydrolysed.

Q.5. BF_3 can act as Lewis acid but CCl_4 cannot do so. Why ?

Ans. BF_3 molecule can act as a Lewis acid because it can accept a pair of electrons from electron donor groups and thus completes its octet. But in CCl_4, carbon atom has already got a complete octet so it cannot accept a pair of electrons. Hence, it does not act as a Lewis acid.

Q.6. AlF_3 is high melting solid but $AlCl_3$ is low melting. Explain.

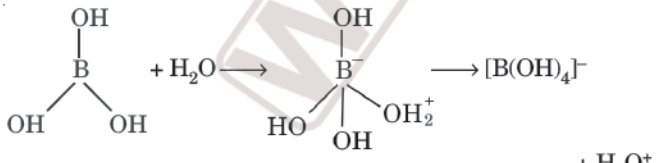
Ans. AlF_3 is high melting solid because it is ionic in nature. On the other hand, $AlCl_3$ is covalent in nature and hence is a low melting solid.

Q.7. Account for the dimeric structure of $AlCl_3$.

Ans. The molecular formula of aluminium chloride is $AlCl_3$. In aqueous solution, it exists in monomeric form. But in vapour state, it exists as a dimer, Al_2Cl_6. In this structure, the Al atom of one $AlCl_3$ unit accepts a lone pair of electrons from a Cl atom of the second $AlCl_3$ molecule. In this way, the octet of each Al atom is completed as :

Q.8. Boric acid is monobasic. Explain.

Ans. Boric acid $B(OH)_3$ acts as an acid by accepting OH^- ion (Lewis acid).



Boron thus forms $[B(OH)_4]^-$ ion and completes its octet. Therefore, it acts as a monobasic acid because there is no provision for further reaction since boron atom has completed its octet.

Q.9. Boric acid can be titrated against sodium hydroxide using methyl orange as indicator only in the presence of polyhydroxy compounds like catechol, mannitol etc. Explain.

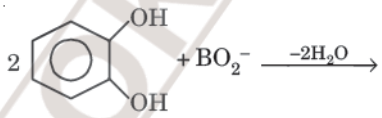
Ans. Boric acid is a weak acid and reacts with NaOH to form sodium metaborate.

$$B(OH)_3 + NaOH \longrightarrow Na^+BO_2^- + 2H_2O$$

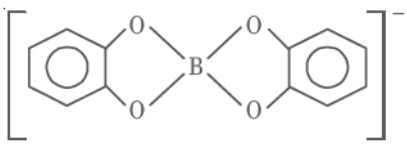
The end point during the titration of H_3BO_3 and NaOH is not sharp and cannot be detected properly. This is because of the fact that sodium metaborate formed during the neutralisation reaction undergoes hydrolysis and gives back H_3BO_3 and NaOH.

$$NaBO_2 + 2H_2O \rightleftharpoons B(OH)_3 + NaOH$$

However, when titration is carried out in the presence of certain polyhydroxy compounds such as catechol $[C_6H_4(OH)_2]$, mannitol $[C_6H_8(OH)_6]$, glycerol $[CH_2OHCH(OH)\,CH_2OH]$ etc. boric acid behaves as a strong monobasic acid and end point can be detected easily. The metaborate ion combines with the polyhydroxy compound to form a complex.



Catechol



Complex ion

The above complex does not combine with H^+ ions because boron atom has acquired the maximum covalency of four. Therefore, BO_2^- does not undergo hydrolysis. As a result, boric acid ionises to greater extent producing large number of H^+ ions and therefore, it behaves as a strong acid and can be easily titrated with NaOH.

Q.10. PbO_2 is a stronger oxidising agent than SnO_2. Explain.

Ans. In PbO_2 and SnO_2, both lead and tin are present in +4 oxidation state. But lead shows stronger inert pair effect so that Pb^{2+} ion is more stable than Pb^{4+} ion whereas Sn^{4+} ion is more stable than Sn^{2+} ion. Therefore, Pb^{4+} ions (PbO_2) are more readily reduced to Pb^{2+} ions as compared to Sn^{4+}. Thus, PbO_2 acts as a stronger oxidising agent.

Q.11. Molten aluminium bromide is a poor conductor of electricity. Why ?

Ans. Aluminium bromide is a covalent molecule. Even in molten state it, ionizes only to a very small extent and therefore, is a poor conductor of electricity.

Q.12. Like CO, its analog SiO is not stable. Why ?

Ans. CO is a resonance hybrid of the following structures:

Therefore, CO has $p\pi$–$p\pi$ multiple bonds. This is because C being small in size and having high electronegativity forms strong $p\pi$–$p\pi$ bonds. Silicon on the other hand, because of its larger size and lower electronegativity has no tendency to form $p\pi$–$p\pi$ bonds and hence does not form stable SiO.

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Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. What is the formula of kernite, an ore of boron ?
2. What is borax bead test ?
3. What is the action of heat on boric acid ?
4. Why does boron halides form addition compounds with amines ?
5. Why do boron halides behave as Lewis acids ?
6. What is the shape of BH_4^- ion ?
7. Which is the most aboundant element in group 13 ?
8. What are the formulae of bauxite and cryolite ?
9. Which of the two Al and Ga has larger atomic radius ?
10. Why does $AlCl_3$ exists as dimer ?
11. Is B_2O_3 acidic or basic oxide ?
12. What happen when borax is heated ?
13. Name the second most abundant element on the earth's crust.
14. What type of hybridisation of central atom is possible in $[GeCl_6]^{2-}$?
15. Name the member of group 14 that forms the most acidic oxide.
16. Complete the reaction :

    Sn + steam $\longrightarrow$
17. Which of the two allotropes : diamond or graphite is good conductor of electricity and why ?
18. Diamond is a covalent compound, yet it has high melting point. Why ?
19. How is producer gas prepared ?
20. Write the resonating structures of CO_2.
21. Write the structure of basic unit of all silicates.
22. Define inert pair effect.
23. Is boric acid a protic acid ? Explain.
24. Why does BF_3 behave as a Lewis acid ?
25. Explain what happens when boric acid is added to water ?
26. Though B-Cl bond is polar yet BCl_3 has zero dipole moment. Explain.
27. Suggest reason as to why CO is poisonous.
28. Why do boron halides form addition compounds with amines ?
29. What is dry ice ? Why is it so called ?
30. Describe what happens when boric acid is heated ?

Short Answer Questions *Carrying 2 or 3 marks*

1. Explain why are boron halides referred to as electron deficient compounds.
2. How does boron react with

   (*i*) NaOH (*ii*) N_2 ?
3. By means of a balanced equation show how $B(OH)_3$ behaves as an acid in water.
4. What are fullerenes ? How are they prepared ?
5. Write resonance structures for CO_3^{2-} and HCO_3^-.
6. Account for the toxic nature of carbon monoxide.
7. Explain the differences in the properties of diamond and graphite on the basis of their structures.
8. Write brief account of water gas and producer gas.
9. How is borax prepared from colamanite ? How does it react with water ? Give the chemistry of borax bead test.
10. How is boric acid prepared from borax ? Discuss its structure.
11. How would you explain the lower atomic radius of Ga as compared to Al ?
12. How does BF_3 react with

    (*i*) ammonia (*ii*) lithium hydride

    (*iii*) water
13. Comment on the $p\pi$-$p\pi$ and dπ-$p\pi$ bonding in elements of group 14.
14. List some important consequences of absence of *d*-orbitals in boron and carbon.
15. Give four important uses of each of the following :

    (*i*) Aluminium (*ii*) Carbon
16. In some reactions, thallium resembles aluminium whereas in others it resembles with group I metals. Support this statement by giving some evidences.
17. Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon ?
18. Discuss the pattern of variation in oxidation states of

    (*i*) B to Tl (*ii*) C to Pb
19. Write reactions to account for amphoteric nature of aluminium.
20. Explain structures of diborane and boric acid.
21. Suggest reasons why the B-F bond lengths in BF_3 is smaller than in BF_4^-.
22. What is the state of hybridisation of carbon in

    (*i*) CO_3^{2-} (*ii*) diamond

    (*iii*) graphite (*iv*) CCl_4
23. Describe the shapes of following :

    (*i*) BF_4^- (*ii*) BCl_3

    (*iii*) Al_2Cl_6 (*iv*) $SiCl_4$

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24. How can you explain the stability of BCl_3 as compared to $TlCl_3$?

25. Classify the following oxides as neutral, acidic or amphoteric or basic ?

(*i*) CO (*ii*) B_2O_3 (*iii*) SiO_2 (*iv*) CO_2

(*v*) Al_2O_3 (*vi*) PbO_2 (*vii*) Tl_2O_3

26. Discuss the variation of following properties in group 13 :

(*i*) reactivity with air

(*ii*) reactivity with acids and alkalies

(*iii*) reactivity towards hologens.

27. Explain the following :

(*i*) Boron does not form BF_6^{3-}.

(*ii*) Boric acid is a weak acid.

(*iii*) BF_3 is weaker Lewis acid than BCl_3.

(iv) $[SiF_6]^{2-}$ is known but $[SiCl_6]^{2-}$ is not.

28. Discuss the following among group 14 elements :

(*i*) Oxidation states

(*ii*) Atomic size

(*iii*) Reactivity with oxygen

29. Complete the following reactions :

(*i*) $Na_2B_4O_7\,10H_2O \xrightarrow{\text{Heat}}$

(*ii*) $H_3BO_3 + H_2O \longrightarrow$

(*iii*) $Fe_2O_3 + CO \longrightarrow$

(*iv*) $HCOOH \xrightarrow{\text{Heat}}$

(*v*) $BN + H_2O \longrightarrow$

Long Answer Questions *Carrying 5 marks*

1. Describe the structure of diborane. What is special about this structure ?

2. Write short notes on :

(*i*) Fullerenes (*ii*) Structure of graphite

(*iii*) Structure of diborane

3. Name the elements of group 14. Discuss the variation in characteristics of the group with reference to

(*a*) Oxidation state (*b*) Catenation

(*c*) Metallic character (*d*) Reactivity with oxygen

4. Explain the following :

(*a*) $PbCl_4$ is less stable than $PbCl_2$

(*b*) Tl(I) compounds are more stable than Tl(III)

(*c*) CO_2 is a gas while SiO_2 is a solid.

(*d*) $AlCl_3$ exists as dimer but BCl_3 does not.

(*e*) BF_3 is less Lewis acid than BCl_3.

(*f*) Boric acid is not protic acid.

5. How do you account for

(*i*) Anhydrous $AlCl_3$ is covalent but hydrated $AlCl_3$ is ionic.

(*ii*) BBr_3 is stronger lewis acid than BF_3.

(*iii*) Boron does not form B^{3+} ions.

6. Write balanced chemical equations for :

(*i*) $SiO_2 + HF \longrightarrow$

(*ii*) $AlCl_3 + NaOH \longrightarrow$

(*iii*) $Na_2B_4O_7 + H_2O \longrightarrow$

(*iv*) $BF_3 + LiAlH_4 \longrightarrow$

(*v*) $BH_3 + CO \longrightarrow$

7. Write a brief account of

(*a*) structure of diborane

(*b*) silicones and their uses

(*c*) uses of aluminium

Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

CARBIDES

Carbon combines with many electropositive elements when heated to high temperature to form carbides. The **carbides** *are compounds of carbon with more electropositive elements than itself.* Some common examples are silicon carbide (SiC), iron carbide (Fe_3C), calcium carbide (CaC_2), tungsten carbide (WC), aluminium carbide (Al_4C_3) etc.

Carbides can be classified on the basis of type of bonding in them as :

(*a*) Ionic carbides : These are the carbides of strongly electropositive metals belonging to the alkali and alkaline earth metals and aluminium. For example, CaC_2, Al_4C_3, Mg_2C_3, Be_2C, etc.

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These are essentially ionic in nature. These are easily hydrolysed with water or dilute acids at ordinary temperatures forming hydrocarbons corresponding to the anions C^{4-}(CH_4), C_2^{2-} (C_2H_2) and C_3^{4-}(C_3H_4). Depending upon the hydrocarbon which they form on hydrolysis, these carbides are classified as :

(*i*) Methanides. These contain individual carbon anions (C^{4-}) and give methane on hydrolysis.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$
$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

(*ii*) Acetylides. These contain the carbide anion C_2^{2-} $(-C\equiv C^-)^{2-}$ and give acetylene on hydrolysis. For example, MgC_2, CaC_2 etc.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

(*iii*) Allylides. These contain C_3^{4-} anion and give allylene on hydrolysis. For example,

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + \underset{\text{Allylene}}{CH_3-C\equiv CH}$$

CaC_2, Al_4C_3, Mg_2C_3, etc.

(*b*) Covalent carbides : These are the compounds of carbon with metalloids which have the same electronegativity as carbon. For example, silicon carbide (SiC), boron carbide (B_4C). Silicon carbide is known as **carborundum** and is used for making cutting tools and abrasives.

Boron carbide is also extremely hard and is used as an abrasive and as an shield from radiation. It is prepared by the reduction of B_2O_3 with C in an electric furnace at 2773 K.

(*c*) Interstitial carbides : These are the compounds of carbon with transition metals and some of the lanthanides and actinides *e.g.*, WC, TaC, ZrC, V_2C, etc.

In these compounds, the carbon atoms occupy the voids in the close packed lattice of metal atoms. These carbides are extremely hard and electrically conducting. Due to their extremely hardness and inertness, WC and TaC are used for the manufacture of high speed cutting and drilling tools.

Carbides are generally prepared by heating the element or its oxide with carbon at a very high temperature. For example,

Applications of carbides. Carbides have many applications in industry. Some of these are :

(*i*) Silicon carbide known as *carborundum* is very hard and is used as an abrasive for sharpening and grinding metals and other substances.

(*ii*) Tungsten carbide is used for making tools and dies.

(*iii*) Calcium carbide is used for preparing acetylene which is used for welding and is an important starting material for a number of organic compounds such as ethyl alcohol, acetic acid, etc.

(*iv*) Be_4C is also very hard and is used as a shield against radioactive radiations.

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answer :

GROUP 13 ELEMENTS

A1. Borax gets hydrolysed to give
(*a*) basic medium
(*b*) acidic medium
(*c*) neutral medium
(*d*) may be acidic or neutral.

A2. Orthoboric acid on strong heating to red hot gives
(*a*) Metaboric acid (*b*) Borax
(*c*) Boron trioxide (*d*) Tetraboric acid.

A3. The most basic oxide is
(*a*) B_2O_3 (*b*) Ga_2O_3
(*c*) Tl_2O_3 (*d*) Al_2O_3

A4. An aqueous solution of borax is
(*a*) bleaching agent (*b*) alkaline
(*c*) acidic (*d*) neutral.

A5. Three centre two electron bond is present is
(*a*) BF_3 (*b*) B_2H_6
(*c*) H_3BO_3 (*d*) $AlCl_3$

A6. From B_2H_6, all the following can be prepared except
(*a*) $B_2(CH_3)_6$ (*b*) H_3BO_3
(*c*) $B_2(CH_3)_4H_2$ (*d*) $B_3N_3H_6$

A7. Among the following the compound which exists as dimer is
(*a*) BCl_3 (*b*) $AlCl_3$
(*c*) $CHCl_3$ (*d*) CO_2

A8. Which of the following has least Lewis acid character ?
(*a*) BI_3 (*b*) BCl_3
(*c*) BBr_3 (*d*) BF_3

A9. $AlCl_3$ dissolves in NaOH to form
(*a*) Al_2O_3 (*b*) $Na[Al(OH)_4]$
(*c*) $Na_3[Al(OH)_6]$ (*d*) Na_3AlO_3

A10. In Al_2Cl_6, the number σ and coordinate bonds are :
(*a*) 3, 3 (*b*) 2, 4
(*c*) 4, 2 (*d*) 6, 0

A11. The hydrolysis of diborane gives a solution which is
(*a*) neutral (*b*) basic
(*c*) acidic (*d*) amphoteric

Answers

A1. (*a*) **A2.** (*c*) **A3.** (*c*) **A4.** (*b*) **A5.** (*b*) **A6.** (*a*) **A7.** (*b*) **A8.** (*d*) **A9.** (*b*) **A10.** (*c*) **A11.** (*c*)

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A12. The type of hybridisation in diborane is
(a) sp (b) sp^2
(c) sp^3 (d) dsp^2

A13. Boric acid is polymeric due to
(a) its acidic nature
(b) the presence of hydrogen bonds
(c) its monomeric nature
(d) its geometry

A14. B_2O_3 is
(a) acidic (b) basic
(c) neutral (d) amphoteric

A15. Borax is prepared by treating colemanite with
(a) $NaNO_3$ (b) NaCl
(c) Na_2CO_3 (d) $NaHCO_3$.

A16. Which of the following statement about boric acid is false ?
(a) It acts as a monobasic acid
(b) It is formed by the hydrolysis of boron halides
(c) It has planar structure.
(d) It acts as a tribasic acid.

A17. The geometry and type of hybrid orbitals present about the central atom in BF_3 is
(a) linear, sp (b) trigonal planar sp^2
(c) tetrahedral, sp^3 (d) pyramidal sp^3

A18. Which of the following is not a protonic acid ?
(a) $B(OH)_3$ (b) $PO(OH)_3$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

A19. Borax is used as cleansing agent because on dissolving in water it gives
(a) alkaline solution
(b) acidic solution
(c) bleaching solution
(d) colloidal solution

A20. Al_2O_3 can be converted to anhydrous $AlCl_3$ by heating
(a) Al_2O_3 with NaCl in solid state
(b) a mixture of Al_2O_3 and carbon in dry Cl_2 gas
(c) Al_2O_3 with Cl_2 gas
(d) Al_2O_3 with HCl gas

GROUP 14 ELEMENTS

A21. Carborundum is
(a) Calcium carbide (b) Boron carbide
(c) Aluminium carbide (d) Silicon carbide

A22. Carbon forms large number of compounds because it has
(a) low electron affinity
(b) no d-orbitals in valence shell
(c) variable valency
(d) property of catenation

A23. When formic acid is heated, the gas evolved is
(a) CO (b) CO_2
(c) H_2 (d) SO_2

A24. Inert pair effect is predominant in
(a) Si (b) Pb
(c) Ge (d) Sn

A25. Silicon shows diagonal relationship with
(a) B (b) Be
(c) C (d) Al

A26. The high temperature polymers of silicon are called
(a) Silicates (b) Silicon halides
(c) Silanes (d) Silicones

A27. Which of the following is not the from of silica ?
(a) Cassiterite (b) Cristobalite
(c) Tridymite (d) Quartz

A28. Which of the following species does not exist ?
(a) $[SnCl_6]^{2-}$ (b) $[SiCl_6]^{2-}$
(c) $[CCl_6]^{2-}$ (d) $[GeCl_6]^{2-}$

A29. The basic structural unit of silicates is
(a) SiO_2 (b) Si^{4+}
(c) SiO_4^{4-} (d) SiO_4^{2-}

A30. Thermodynamically the most stable form of carbon is
(a) diamond (b) graphite
(c) fullerenes (d) coal

A31. Elements of group 14
(a) exhibit oxidation state of + 4 only
(b) exhibit oxidation state of +2 and +4
(c) form M^{2-} and M^{4+} ions
(d) form M^{2+} and M^{4-} ions

A32. Which of the oxide is neutral ?
(a) CO (b) SnO_2
(c) ZnO (d) SiO_2

A33. In graphite, electrons are
(a) localised on every third carbon
(b) present in antibonding orbitals
(c) localised on each carbon atom
(d) spread out between the structure

A34. Percentage of lead in lead pencil is
(a) zero (b) 20
(c) 80 (d) 60

A35. Which of the following is electron deficient molecule ?
(a) C_2H_6 (b) B_2H_6
(c) SiH_4 (d) Al_2Cl_6

A36. Supercritical CO_2 is used as
(a) dry ice (b) fire fighting
(c) a solvent for extraction of organic compounds from natural sources.
(d) a highly inert medium for carrying out various reactions.

Answers

A12. (c)	**A13.** (b)	**A14.** (a)	**A15.** (c)	**A16.** (d)	**A17.** (b)	**A18.** (a)	**A19.** (a)	**A20.** (b)	**A21.** (d)
A22. (d)	**A23.** (a)	**A24.** (b)	**A25.** (a)	**A26.** (d)	**A27.** (a)	**A28.** (c)	**A29.** (c)	**A30.** (b)	**A31.** (b)
A32. (a)	**A33.** (d)	**A34.** (a)	**A35.** (b)	**A36.** (c)					

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B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT & Other State Boards' Medical Entrance

B1. Which one of the following anions is present in the chain structure of silicates ?

(*a*) SiO_4^{4-} (*b*) $Si_2O_7^{6-}$
(*c*) $(Si_2O_5^{2-})_n$ (*d*) $(SiO_3^{2-})_n$

(C.B.S.E. P.M.T. 2007)

B2. The ion(s) that act/s as oxidizing agent in solution is/are :

(*a*) Tl^+ and Al^{3+} (*b*) B^{3+} and Al^{3+}
(*c*) Tl^{3+} only (*d*) B^{3+} only
(*e*) Ti^{3+} only *(Kerala PMT 2008)*

B3. The stability of +1 oxidation state increases in the sequence

(*a*) Tl < In < Ga < Al (*b*) In < Tl < Ga < Al
(*c*) Ga < In < Al < Tl (*d*) Al < Ga < In < Tl

(CBSE-PMT 2009)

B4. The straight chain polymer is formed by

(*a*) hydrolysis of CH_3SiCl_3 followed by condensation polymerisation
(*b*) Hydrolysis of $(CH_3)_4Si$ by addition polymerisation
(*c*) Hydrolysis of $(CH_3)_2SiCl_2$ followed by condensation polymerisation.
(*d*) Hydrolysis of $(CH_3)_3SiCl$ followed by condensation polymerisation. *(CBSE-PMT 2009)*

B5. Reaction of diborane with ammonia gives initially

(*a*) $B_2H_6{\cdot}NH_3$ (*b*) Borazole
(*c*) $B_2H_6.3NH_3$ (*d*) $[BH_2(NH_3)_2]^+[BH_4]^-$
(*e*) $B_2N_4H_{10}$ *(Kerala PMT 2010)*

B6. The correct order of matching of the following compounds is

(A) Borazole (*i*) $CaSO_4.\frac{1}{2}H_2O$
(B) Plaster of Paris (*ii*) C_{60}
(C) Boric acid (*iii*) SiO_2
(D) Quartz (*iv*) $B_3N_3H_6$
(E) Buckminster fullerence (*v*) H_3BO_3

(*a*) A - (*iii*) ; B - (*i*) ; C - (*ii*) ; D - (*v*) ; E - (*iv*)
(*b*) A - (*i*) ; B - (*v*) ; C - (*iii*) ; D - (*iv*) ; E - (*ii*)
(*c*) A - (*v*) ; B - (*ii*) ; C - (*i*) ; D - (*iii*) ; E - (*iv*)
(*d*) A - (*iv*) ; B - (*i*) ; C - (*v*) ; D - (*iii*) ; E - (*ii*)
(*e*) A - (*iv*) ; B - (*i*) ; C - (*v*) ; D - (*ii*) ; E - (*iii*)

(Kerala PMT 2010)

B7. $B(OH)_3$ is a

(*a*) Lewis acid (*b*) Lewis base
(*c*) Bronsted base (*d*) Bronsted acid
(*e*) Neutral compound

(Kerala PMT 2010)

B8. Germanium of very high purity is obtained by

(*a*) liquation (*b*) vapour phase refining
(*c*) distillation (*d*) zone refining
(*e*) electrolytic refining *(Kerala P.M.T. 2012)*

B9. The product/s formed when diborane is hydrolysed is/are

(*a*) B_2O_3 and H_3BO_3 (*b*) B_2O_3 only
(*c*) H_3BO_3 and H_2 (*d*) H_3BO_3 only
(*e*) B_2O_3 and H_2 *(Kerala P.M.T. 2012)*

B10. The basic structural unit of silicates is

(*a*) SiO_3^{2-} (*b*) SiO_4^{2-}
(*c*) SiO^- (*d*) SiO_4^{4-} (NEET 2013)

B11. Which of these is not a monomer for a high molecular mass silicone polymer ?

(*a*) Me_3SiCl (*b*) $PhSiCl_3$
(*c*) $MeSiCl_3$ (*d*) Me_2SiCl_2 *(NEET 2013)*

B12. Three centred two electron bond is present in

(*a*) NH_3 (*b*) B_2H_6
(*c*) BCl_3 (*d*) $AlCl_3$
(*e*) BF_3 *(Kerala PMT 2014)*

B13. The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence:

(*a*) Ti < In < Ga < Al (*b*) In < Tl < Ga < Al
(*c*) Ga < In < Al < Tl (*d*) Al < Ga < In < Tl

(AIPMT 2015)

B14. Which of the following fluoro-compound is most likely to behave as a Lewis base?

(*a*) BF_3 (*b*) PF_3
(*c*) CF_4 (*d*) SiF_4 *(NEET 2016)*

B15. Boric acid is an acid because its molecule

(*a*) contains replaceable H^+ ion
(*b*) gives up a proton
(*c*) accepts OH^- from water releasing proton
(*d*) combines with proton from water molecule

(NEET 2016)

B16. It is because of inability of ns^2 electrons of the valence shell to participate in bonding that

(*a*) Sn^{2+} is oxidising while Pb^{4+} is reducing
(*b*) Sn^{2+} and Pb^{2+} are both oxidising and reducing
(*c*) Sn^{4+} is reducing while Pb^{4+} is oxidising
(*d*) Sn^{2+} is reducing while Pb^{4+} is oxidising

(NEET 2017)

Answers

B1. (*d*) **B2.** (*c*) **B3.** (*d*) **B4.** (*d*) **B5.** (*d*) **B6.** (*d*) **B7.** (*a*) **B8.** (*d*) **B9.** (*c*) **B10.** (*d*)
B11. (*a*) **B12.** (*b*) **B13.** (*d*) **B14.** (*b*) **B15.** (*c*) **B16.** (*d*)

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B17. Which one of the following element is unable to form MF_6^{3-} ion?
(a) Ga (b) Al
(c) B (d) In *(NEET 2018)*

B18. The correct order of atomic radii in group 13 elements is
(a) B < Al < In < Ga < Tl
(b) B < Al < Ga < In < Tl
(c) B < Ga < Al < Tl < In
(d) B < Ga < Al < In < Tl *(NEET 2018)*

JEE (Main) & Other State Boards' Engineering Entrance

B19. Graphite is soft and lubricant extremely difficult of melt. The reason for this anomalous behaviour is that graphite
(a) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds.
(b) is a non-crystalline substance
(c) is an allotrope form of carbon
(d) has molecules of variable molecular masses like polymers. *(A.I.E.E.E. 2003)*

B20. Which one of the following has regular tetrahedral structure ?
(a) BF_4^- (b) SF_4
(c) XeF_4 (d) $[Ni(CN)_4]^{2-}$ *(A.I.E.E.E. 2004)*

B21. Which of the following oxide is amphoteric in character ?
(a) CaO (b) CO_2
(c) SiO_2 (d) SnO_2 *(A.I.E.E.E. 2005)*

B22. Heating an aqueous solution of aluminium chloride to dryness will give
(a) $AlCl_3$ (b) Al_2Cl_6
(c) Al_2O_3 (d) $Al(OH)Cl_2$ *(A.I.E.E.E. 2005)*

B23. In silicon dioxide
(a) each silicon atom is surrounded by four oxygen atoms and each oxygen atoms is bonded to two silicon atoms
(b) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms.
(c) silicon atom is bonded to two oxygen atoms
(d) there are double bonds between silicon and oxygen atoms *(A.I.E.E.E. 2005)*

B24. The structure of diborane (B_2H_6) contains
(a) four *2c–2e* bonds and two *3c–2e* bonds
(b) two *2e–2e* bonds and four *3c–3e* bonds
(c) two *2e–2e* bonds and four *3e–2e* bonds.
(d) four *2e–2e* bonds and four *3e–2e* bonds. *(A.I.E.E.E. 2005)*

B25. When PbO_2 reacts with conc. HNO_3, the gas envolved is
(a) NO_2 (b) O_2
(c) N_2 (d) N_2O *(A.I.E.E.E. 2005)*

B26. A metal M forms two chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct ?
(a) MCl_2 is more soluble in anhydrous ethanol than MCl_4.
(b) MCl_2 is more ionic than MCl_4.
(c) MCl_2 is more easily hydrolysed than MCl_4.
(d) MCl_2 is more volatile than MCl_4. *(A.I.E.E.E. 2006)*

B27. The stability of the dihalides of Si, Ge, Sn and Pb increases steadily in the sequence :
(a) $SiX_2 << GeX_2 << PbX_2 << SnX_2$
(b) $SiX_2 << GeX_2 << SnX_2 << PbX_2$
(c) $PbX_2 << SnX_2 << GeX_2 << SiX_2$
(d) $GeX_2 << SiX_2 << SnX_2 << PbX_2$ *(A.I.E.E.E. 2007)*

B28. Diamond is hard because
(a) All the four valence electrons are bonded to each carbon atom by covalent bonds
(b) It is a giant molecule
(c) It is made up of carbon atoms
(d) It cannot be burnt *(A.I.E.E.E. 2008)*

B29. Which one of the following is the correct statement ?
(a) B_2H_6. $2NH_3$ is known as 'inorganic benzene'
(b) Boric acid is a protonic acid
(c) Beryllium exhibits coordination number of six
(d) Chlorides of both beryllium and aluminium have bridged chloride structures in the solid phase. *(A.I.E.E.E. 2008)*

B30. Which one of the following has highest Lewis acid strength ?
(a) BI_3 (b) BBr_3
(c) BF_3 (d) BCl_3 *(J & K 2009)*

B31. The basic structural unit in silicates is
(a) SiO_2 (b) SiO_4^{4-} tetrahedron
(c) $[Si_2O_7]^{2-}$ (d) $[Si_2O_5]^{2-}$ *(AMU-Engg. 2009)*

B32. The products of the following reaction?
$SiO_2 + C \xrightarrow{\Delta}$ are :
(a) SiC and CO_2 (b) SiO and CO
(c) SiC and CO (d) Si and CO_2 *(Orissa JEE 2010)*

Answers

B17. (c) **B18.** (d) **B19.** (a) **B20.** (a) **B21.** (d) **B22.** (b) **B23.** (a) **B24.** (a) **B25.** (b) **B26.** (b)
B27. (b) **B28.** (a) **B29.** (d) **B30.** (a) **B31.** (b) **B32.** (c)

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B33. Which of the following is not hydrolysed easily ?
(*a*) CCl_4 (*b*) $SiCl_4$
(*c*) $GeCl_4$ (*d*) $SnCl_4$ *(Orissa JEE 2010)*

B34. Which of the following is non-existent ?
(*a*) AlF_6^{3-} (*b*) CoF_6^{3-}
(*c*) BF_6^{3-} (*d*) SiF_6^{2-} *(AMU Engg. 2010)*

B35. Which of the following has least tendency to undergo catenation ?
(*a*) C (*b*) Si
(*c*) Ge (*d*) Sn *(AMU Engg. 2010)*

B36. The strongest Lewis acid among boron halides is
(*a*) BBr_3 (*b*) BCl_3
(*c*) BI_3 (*d*) BF_3 *(AMU Engg. 2010)*

B37. Boron cannot form which one of the following anions ?
(*a*) BF_6^{3-} (*b*) BH_4^-
(*c*) $B(OH)_4^-$ (*d*) BO_2^- *(AIEEE 2011)*

B38. In diborane (B_2H_6), there are
(*a*) three $3c - 2e^-$ bonds and three $2c - 2e^-$ bonds
(*b*) four $3c - 2e^-$ bonds and two $2c - 2e^-$ bonds
(*c*) two $3c - 2e^-$ bonds and four $2c - 2e^-$ bonds
(*d*) none of the above *(AMU Engg. 2011)*

B39. The stable bivalency of Pb and trivalency of Bi is
(*a*) due to d contraction in Pb and Bi
(*b*) due to relativistic contraction of the 6*s* orbitals of Pb and Bi, leading to inert pair effect
(*c*) due to screening effect
(*d*) due to attainment of noble configuration
(W.B.J.E.E. 2012)

B40. The correct order of decreasing Lewis acidity is
(*a*) $BF_3 > BCl_3 > BBr_3 > BI_3$
(*b*) $BI_3 > BCl_3 > BBr_3 > BF_3$
(*c*) $BI_3 > BBr_3 > BCl_3 > BF_3$
(*d*) $BCl_3 > BF_3 > BBr_3 > BI_3$ *(J.K.C.E.T 2012)*

B41. Boron is unable to form BF_6^{3-} because of
(*a*) high electronegativity of boron
(*b*) high electronegativity of fluorine
(*c*) lack of *d*-orbitals in boron
(*d*) less difference in electronegativity between B and F. *(J.K.C.E.T. 2012)*

B42. The most stable oxidation state exhibited by thallium is
(*a*) 0 (*b*) +1
(*c*) +2 (*d*) +3 *(J.K.C.E.T. 2012)*

B43. In diborane, the number of electrons that account for bonding in the bridges is
(*a*) six
(*b*) two
(*c*) eight
(*d*) four *(W.B.JEE 2013)*

B44. For BCl_3, $AlCl_3$ and $GaCl_3$ the increasing order of ionic character is
(*a*) $BCl_3 < AlCl_3 < GaCl_3$
(*b*) $GaCl_3 < AlCl_3 < BCl_3$
(*c*) $BCl_3 < GaCl_3 < AlCl_3$
(*d*) $AlCl_3 < BCl_3 < GaCl_3$ *(W.B.JEE 2013)*

B45. In borax, the number of B – O – B links and B – OH bonds present are respectively
(*a*) five and four (*b*) four and five
(*c*) three and four (*d*) five and five
(W.B.JEE 2013)

B46. Silicone oil is obtained from the hydrolysis and polymerization of
(*a*) trimethylchlorosilane and dimethyldichlorosilane
(*b*) trimethylchlorosilane and methyltrichlorosilane
(*c*) methyltrichlorosilane and dimethyldichlorosilane
(*d*) triethylchlorosilane and diethyldichlorosilane
(W.B.JEE 2013)

B47. Among the elements B, Mg, Al and K, the correct order of increasing metallic character is
(*a*) B < Al < Mg < K
(*b*) B < Mg < Al < K
(*c*) Mg < B < Al < K
(*d*) Mg < Al < B < K
(*e*) K < Mg < Al < B *(Kerala P.E.T. 2013)*

B48. The correct formula of borax is
(*a*) $Na_2[B_4O_4(OH)_3].9\,H_2O$
(*b*) $Na_2[B_4O_5(OH)_4].8\,H_2O$
(*c*) $Na_2[B_4O_6(OH)_5].7\,H_2O$
(*d*) $Na_2[B_4O_7(OH)_6].6\,H_2O$
(*e*) $Na_2[B_4O_8(OH)_7].5\,H_2O$ *(Kerala P.E.T. 2013)*

B49. The +1 oxidation state of thallium is more stable than its + 3 oxidation state because of
(*a*) its atomic size
(*b*) its ionisation potential
(*c*) inert pair effect
(*d*) diagonal relationship *(J.K. C.E.T. 2013)*

B50. For the properties mentioned, the correct trend for the different species is in
(*a*) strength as Lewis acid – $BCl_3 > AlCl_3 > GaCl_3$
(*b*) inert pair effect – Al > Ga > In
(*c*) oxidising property – $Al^{3+} > In^{3+} > Tl^{3+}$
(*d*) first ionization enthalpy – B > Al > Tl
(Karnataka CET 2014)

B51. Which one of the following metallic oxides exhibit amphoteric nature ?
(*a*) BaO (*b*) Al_2O_3
(*c*) Na_2O (*d*) CaO
(Karnataka CET 2017)

Answers

B33. (*a*) **B34.** (*c*) **B35.** (*d*) **B36.** (*c*) **B37.** (*a*) **B38.** (*c*) **B39.** (*b*) **B40.** (*c*) **B41.** (*c*) **B42.** (*b*)
B43. (*d*) **B44.** (*c*) **B45.** (*a*) **B46.** (*a*) **B47.** (*a*) **B48.** (*b*) **B49.** (*c*) **B50.** (*a*) **B51.** (*b*)

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B52. Addition of mineral acid to an aqueous solution of borax, the following compound is formed:
(*a*) boron hydride (*b*) pyroboric acid
(*c*) metaboric acid (*d*) orthoboric acid
(Karnataka CET 2017)

B53. $(CH_3)_3SiCl$ is used during polymerisation of organosilicons because
(*a*) the chain length of organosilicon polymers can be controlled by adding $(CH_3)_3$ SiCl
(*b*) $(CH_3)_3$ SiCl improves the quality and yield of the polymer.
(*c*) $(CH_3)_3$ SiCl does not block the end terminal of silicone polymer.
(*d*) $(CH_3)_3SiCl$ acts as a catalyst during polymerisation. *(Karnataka CET 2018)*

B54. $Al_2(SO_4)_3$ is used in the following but not
(*a*) as a coagulant in treating drinking water and sewage
(*b*) in plastic industry
(*c*) as a mordant in dyeing
(*d*) in paper industry
(*e*) both (*c*) and (*d*). *(Kerala PET 2018)*

B55. More than four bonds are made by how many elements in carbon family?
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4
(*e*) 5 *(Kerala PET 2017)*

B56. The main reason that $SiCl_4$ is easily hydrolysed as compared to CCl_4 is that
(*a*) Si—Cl bond is weaker than C—Cl bond
(*b*) $SiCl_4$ can form hydrogen bonds
(*c*) $SiCl_4$ is covalent
(*d*) Si can extend its coordination number beyond four. *(WB JEE 2018)*

B57. Which of the set of oxides are arranged in the proper order of basic, amphoteric, acidic?
(*a*) SO_2, P_2O_5, CO (*b*) BaO, Al_2O_3, SO_2
(*c*) CaO, SiO_2, Al_2O_3 (*d*) CO_2, Al_2O_3, CO
(WB JEE 2018)

B58. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is:
(*a*) Zn (*b*) Ca
(*c*) Al (*d*) Fe
(JEE Main 2018)

B59. Aluminium is usually found in +3 oxidation state. In contrast thallium exists in +1 and +3 oxidation states. This is due to
(*a*) lanthanoid contraction
(*b*) lattice effect
(*c*) diagonal relationship
(*d*) inert pair effect *(JEE Main 2019)*

B60. The electronegativity of aluminium is similar to
(*a*) Boron (*b*) Carbon
(*c*) Lithium (*d*) Beryllium
(JEE Main 2019)

B61. The element that shows greater ability to form $p\pi - p\pi$ multiple bond is
(*a*) Si (*b*) Ge
(*c*) Sn (*d*) C *(JEE Main 2019)*

B62. The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6, respectively, are
(*a*) 2 and 4 (*b*) 2 and 1
(*c*) 2 and 2 (*d*) 4 and 2
(JEE Main 2019)

B63. The chloride that cannot get hydrolysed is
(*a*) $SiCl_4$ (*b*) $SnCl_4$
(*c*) $PbCl_4$ (*d*) CCl_4
(JEE Main 2019)

JEE (Advance) for IIT Entrance

B64. $B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$
To keep the reaction in the forward direction, which reagent should be used ?
(*a*) *cis*-1, 2-diol (*b*) *trans*-1, 2-diol
(*c*) borax (*d*) Na_2HPO_4 *(I.I.T. 2006)*

B65. When CO_2 is passed through water, which of the following species will be present in water ?
(*a*) $H_2CO_3, CO_2, CO_3^{2-}, HCO_3^-$
(*b*) HCO_3^-, CO_3^{2-}
(*c*) CO_3^{2-}, CO_2
(*d*) H_2CO_3, CO_2 *(I.I.T. 2006)*

B66. A colourless aqueous solution on adding water and on heating gave a white precipitate. This precipitate when reacted with NH_4Cl and NH_4OH in excess resulted in dissolution of some of the precipitate and a gelatinous precipitate is obtained. What is the hydroxide formed in aqueous solution ?
(*a*) $Zn(OH)_2$ (*b*) $Mg(OH)_2$
(*c*) $Al(OH)_3$ (*d*) $Ca(OH)_2$ *(I.I.T. 2006)*

B67. The increasing order of atomic radii of the following group 13 elements is
(*a*) Al < Ga < In < Tl (*b*) Ga < Al < In < Tl
(*c*) Al < In < Ga < Tl (*d*) Al < Ga < Tl < In
(JEE Advance 2016)

Answers

B52. (*d*) **B53.** (*a*) **B54.** (*b*) **B55.** (*d*) **B56.** (*d*) **B57.** (*b*) **B58.** (*c*) **B59.** (*d*) **B60.** (*d*) **B61.** (*d*)
B62. (*d*) **B63.** (*d*) **B64.** (*a*) **B65.** (*a*) **B66.** (*c*) **B67.** (*b*)

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C MULTIPLE CHOICE QUESTIONS *with more than one correct answers*

C1. Boron trifluoride is
(*a*) electron precise molecule
(*b*) electron deficient molecule
(*c*) used as a rocket fuel
(*d*) Lewis acid

C2. Which of the following species are not known ?
(*a*) $[SiCl_6]^{2-}$ (*b*) $[CF_6]^{2-}$
(*c*) $[SiF_6]^{2-}$ (*d*) $[PbCl_6]^{2-}$

C3. In which of the following elements, the lower oxidation state is more stable than the higher ?
(*a*) In (*b*) Pb
(*c*) Sn (*d*) Tl

C4. Which of the following are amphoteric oxides ?
(*a*) Tl_2O (*b*) Al_2O_3
(*c*) Ga_2O_3 (*d*) B_2O_3

C5. Which of the following statements are not correct ?
(*a*) Unlike graphite, diamond is a good conductor of electricity.
(*b*) Graphite can act as lubricant.
(*c*) Graphite is a black substance and possesses a metallic lustre.
(*d*) C in diamond involves sp^2 hybridisation.

C6. Which of the following examples are correct for silicates ?
(*a*) Orthosilicates : zircon
(*b*) Chain silicates : thortveitite
(*c*) Pyrosilicates : hemimorphite
(*d*) Ring silicate : forestrite

C7. The correct statement(s) for orthoboric acid is/are
(*a*) it behaves as a weak acid in water due to self ionization
(*b*) acidity of its aqueous solution increases upon addition of ethylene glycol
(*c*) it has a three dimensional structure due to hydrogen bonding
(*d*) it is a weak electrolyte in water.
(JEE Advance 2014)

C8. The crystalline form of borax has
(*a*) tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit
(*b*) all boron atoms in the same plane
(*c*) equal number of sp^2 and sp^3 hybridised boron atoms
(*d*) one terminal hydroxide per boron atom
(JEE Advance 2016)

C9. Select the most appropriate statement. In BF_3
(*a*) all the bonds are completely ionic
(*b*) the B—F bond is partially ionic
(*c*) B—F bond has partial double bond character
(*d*) bond energy and bond length data indicate single bond character of the B—F bond
(*e*) all the bonds are covalent. *(Kerala PET 2017)*

C10. The option(s) with only amphoteric oxides is(are)
(*a*) Cr_2O_3, BeO, SnO, SnO_2
(*b*) ZnO, Al_2O_3, PbO, PbO_2
(*c*) NO, B_2O_3, PbO, SnO_2
(*d*) Cr_2O_3, CrO, SnO, PbO *(JEE Advance 2017)*

C11. Among the following the correct statement(s) is(are)
(*a*) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure
(*b*) BH_3 has the three-centre two-electron bonds in its dimeric structure
(*c*) the Lewis acidity of BCl_3 is greater than that of $AlCl_3$
(*d*) $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure *(JEE Advance 2017)*

Answers

C1. (*b, d*) **C2.** (*a, b*) **C3.** (*b, d*) **C4.** (*b, c*) **C5.** (*a, d*) **C6.** (*a, c*) **C7.** (*b, d*) **C8.** (*a, c, d*) **C9.** (*c, e*) **C10.** (*a, b*) **C11.** (*a, b, c*)

D MULTIPLE CHOICE QUESTIONS *based on the given passage/comprehension*

Passage-I

The elements of groups 13 and 14 exhibit two types of oxidation states which differ by 2 units. The heavier elements exhibit oxidation state which is two units lower than group oxidation state.

Answer the following questions :

D1. Elements of group 14 exhibit
(*a*) Oxidation state of +2 only
(*b*) Oxidation state of +4 only
(*c*) Oxidation state of both +4 and +2
(*d*) Oxidation state of +4 and +6

D2. The strongest oxidant among the following is
(*a*) GeO_2 (*b*) PbO_2 (*c*) SnO_2 (*d*) SiO_2

D3. Which of the following statement is not correct ?
(*a*) $PbCl_4$ is less stable than $SnCl_4$ but $PbCl_2$ is more stable than $SnCl_2$
(*b*) PbO_2 is stronger oxidant than SnO_2
(*c*) $(SiH)_3N$ is stronger base than $(CH_3)_3N$.
(*d*) Sn(II) is a reducing agent but Pb(II) is not.

Answers

Passage-I **D1.** (*c*) **D2.** (*b*) **D3.** (*c*)

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D4. Which of the following is not correct ?

(*a*) $3Tl^{+}(aq) \longrightarrow 2Tl + Tl^{3+}(aq)$

(*b*) $3In^{+}(aq) \longrightarrow 2In(s) + In^{3+}(aq)$

(*c*) $2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$

(*d*) $Hg_2^{2+} + Sn^{2+} \longrightarrow 2Hg + Sn^{4+}$

Passage-II

Aluminium reacts with sodium hydroxide to give white precipitate (A) which dissolves in excess of NaOH to give a soluble complex (B).

Answer the following questions :

D5. The precipitate A is because of

(*a*) Al_2Cl_6 (*b*) $Al(OH)_3$ (*c*) $AlCl_3$ (*d*) Al_2O_3

D6. The complex B is

(*a*) Al_2O_3 (*b*) $[Al(OH)_4]^-$ (*c*) $Al(OH)_3$ (*d*) $Al_2(OH)_6$

D7. Preicipitate A on heating gives

(*a*) Al_2O_3 (*b*) $Al(OH)_3$ (*c*) Al (*d*) Al_2Cl_6

Answers

Passage-I **D4.** (*a*) **Passage-II** **D5.** (*b*) **D6.** (*b*) **D7.** (*a*)

Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the correct explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT, but reason is INCORRECT.

(*d*) If assertion is INCORRECT, but reason is CORRECT.

(*e*) If both assertion and reason are INCORRECT.

1. Assertion : Boron has low electrical conductivity

Reason : At ordinary temperature, boron behaves as metal.

2. Assertion : Diborane forms two three centred electron pair bonds.

Reason : B_2H_6 does not have sufficient number of electrons to form normal covalent bonds.

3. Assertion : Graphite is soft and a good lubricating agent.

Reason : The successive layers in graphite are held together by weak forces of attraction.

4. Assertion : Diamond is a bad conductor of electricity.

Reason : All C–C bond lengths in diamond are of 154 pm.

5. Assertion : TlCl is more stable than $TlCl_3$.

Reason : + 1 oxidation state of heaviest element is more stable than +3.

6. Assertion : Carbon dioxide has linear geometry involving *sp* hybridisation of C.

Reason : Dry ice is solid CO_2.

7. Assertion : Boron does not form BF_6^{3-} ion while AlF_6^{3-} is known.

Reason : B does not have *d*-orbitals in valence shell while Al has *d*-orbitals in valence shell.

8. Assertion : Boric acid behaves as weak monobasic acid.

Reason : It has only one ionizable hydrogen.

9. Assertion : Glass is not an example of silicates.

Reason : All silicates have tetrahedral SiO_4^{4-} unit.

10. Assertion : Graphite is good conductor of heat and electricity.

Reason : Graphite has π-electrons which are mobile.

11. Assertion : Silicons are water repelling in nature.

Reason : Silicons are organosilicon polymers, which have $(-R_2SiO-)$ as repeating unit.

12. Assertion : If aluminium atoms replace a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires a negative charge.

Reason : Aluminium is trivalent while silicon is tetravalent.

Answers

1. (*c*) **2.** (*a*) **3.** (*a*) **4.** (*b*) **5.** (*a*) **6.** (*b*) **7.** (*a*) **8.** (*c*) **9.** (*d*) **10.** (*a*) **11.** (*b*) **12.** (*a*)

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Competition File

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is
(*a*) B (*b*) Al
(*c*) Ga (*d*) In

2. Which of the following is a Lewis acid ?
(*a*) $AlCl_3$
(*b*) $MgCl_2$
(*c*) $CaCl_2$
(*d*) $BaCl_2$

3. The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in $[Be(OH)_4]^-$ and the geometry of the complex are respectively
(*a*) sp^3, tetrahedral (*b*) sp^3, square planar
(*c*) sp^3d^2, octahedral (*d*) dsp^2, square planar

4. Which of the following oxides is acidic in nature ?
(*a*) B_2O_3 (*b*) Al_2O_3
(*c*) Ga_2O_3 (*d*) In_2O_3

5. The exhibition of highest co-ordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is *not* likely to act as central atom in MF_6^{3-} ?
(*a*) B (*b*) Al
(*c*) Ga (*d*) In

6. Boric acid is an acid because its molecule
(*a*) contains replaceable H^+ ion
(*b*) gives up a proton
(*c*) accepts OH^- from water releasing proton
(*d*) combines with proton from water molecule

7. Catenation, *i.e.*, linking of similar atoms depends on size and electronic configuration of atoms. The tendency of catenation in Group 14 elements follows the order :
(*a*) C > Si > Ge > Sn (*b*) C >> Si > Ge ≈ Sn
(*c*) Si > C > Sn > Ge (*d*) Ge > Sn > Si > C

8. Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding
(*a*) $MeSiCl_3$ (*b*) Me_2SiCl_2
(*c*) Me_3SiCl (*d*) Me_4Si

9. Ionisation enthalpy (Δ_iH_1 kJ mol^{-1}) for the elements of Group 13 follows the order :
(*a*) B > Al > Ga > In > Tl (*b*) B < Al < Ga < In < Tl
(*c*) B < Al > Ga < In > Tl (*d*) B > Al < Ga > In < Tl

10. In the structure of diborane
(*a*) All hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane.
(*b*) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane.
(*c*) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane.
(*d*) All the atoms are in the same plane.

11. A compound X of boron reacts with NH_3 on heating to give another compound Y which is called inorganic benzene. The compound X can be prepared by treating BF_3 with lithium aluminium hydride. The compounds X and Y are represented by the formulas.
(*a*) B_2H_6, $B_3N_3H_6$ (*b*) B_2O_3, $B_3N_3H_6$
(*c*) BF_3, $B_3N_3H_6$ (*d*) $B_3N_3H_6$, B_2H_6

12. Quartz is extensively used as a piezoelectric material, it contains .....
(*a*) Pb (*b*) Si
(*c*) Ti (*d*) Sn

13. The most commonly used reducing agent is
(*a*) $AlCl_3$ (*b*) $PbCl_2$
(*c*) $SnCl_4$ (*d*) $SnCl_2$

14. Dry ice is
(*a*) Solid NH_3 (*b*) Solid SO_2
(*c*) Solid CO_2 (*d*) Solid N_2

15. Cement, the important building material is a mixture of oxides of several elements. Besides calcium, iron and sulphur, oxides of elements of which of the group (*s*) are present in the mixture ?
(*a*) group 2 (*b*) groups 2, 13 and 14
(*c*) groups 2 and 13 (*d*) groups 2 and 14

Answers

1. (*c*)	**2.** (*a*)	**3.** (*a*)	**4.** (*a*)	**5.** (*a*)	**6.** (*c*)	**7.** (*b*)	**8.** (*c*)	**9.** (*d*)	**10.** (*b*)
11. (*a*)	**12.** (*b*)	**13.** (*d*)	**14.** (*c*)	**15.** (*b*)					

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Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

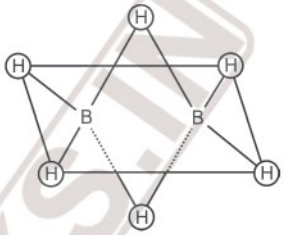
16. The reason for small radius of Ga compared to Al is .....
- (*a*) poor screening effect of *d* and *f* orbitals
- (*b*) increase in nuclear charge
- (*c*) presence of higher orbitals
- (*d*) higher atomic number

17. The linear shape of CO_2 is due to .....
- (*a*) sp^3 hybridisation of carbon
- (*b*) sp hybridisation of carbon
- (*c*) $p\pi - p\pi$ bonding between carbon and oxygen
- (*d*) sp^2 hybridisation of carbon

18. Me_3SiCl is used during polymerisation of organo silicones because
- (*a*) the chain length of organo silicone polymers can be controlled by adding Me_3SiCl
- (*b*) Me_3SiCl blocks the end terminal of silicone polymer
- (*c*) Me_3SiCl improves the quality and yield of the polymer
- (*d*) Me_3SiCl acts as a catalyst during polymerisation

19. Which of the following statements are correct ?
- (*a*) Fullerenes have dangling bonds
- (*b*) Fullerenes are cage-like molecules
- (*c*) Graphite is thermodynamically most stable allotrope of carbon
- (*d*) Graphite is slippery and hard and therefore used as a dry lubricant in machines

20. Which of the following statements are correct. Answer on the basis of figure given below.



- (*a*) The two bridged hydrogen atoms and the two boron atoms lie in one plane
- (*b*) Out of six B–H bonds two bonds can be described in terms of 3 centre 2-electron bonds
- (*c*) Out of six B – H bonds four B – H bonds can be described in terms of 3 centre-2 electron bonds
- (*d*) The four terminal B–H bonds are two centre-two electron regular bonds.

21. Identify the correct resonance structures of carbon dioxide from the following :
- (*a*) O – C ≡ O
- (*b*) O = C = O
- (*c*) $^-O \equiv C - O^+$
- (*d*) $^-O - C \equiv O^+$

Answers

16. (*a*, *b*) **17.** (*b*, *c*) **18.** (*a*, *b*) **19.** (*b*, *c*) **20.** (*a*, *b*, *d*) **21.** (*b*, *d*)

Matching Type Questions

In the following questions more than one correlation is possible between options of Column I and Column II. Make as many correlations as you can.

22. Match the species given in Column I with the properties mentioned in Column II.

Column I	*Column II*
(*i*) BF_4^-	(*a*) Oxidation state of central atom is +4
(*ii*) $AlCl_3$	(*b*) Strong oxidising agent
(*iii*) SnO	(*c*) Lewis acid
(*iv*) PbO_2	(*d*) Can be further oxidised
	(*e*) Tetrahedral shape

23. Match the species given in Column I with properties given in Column II.

Column I	*Column II*
(*i*) Diborane	(*a*) Used as a flux for soldering metals
(*ii*) Galluim	(*b*) Crystalline form of silica
(*iii*) Borax	(*c*) Banana bonds
(*iv*) Aluminosilicate	(*d*) Low melting, high boiling, useful for measuring high temperatures
(*v*) Quartz	(*e*) Used as catalyst in petrochemical industries

24. Match the species given in Column I with the hybridisation given in Column II.

Column I	*Column II*
(*i*) Boron in $[B(OH)_4]^-$	(*a*) sp^2
(*ii*) Aluminium in $[Al(H_2O)_6]^{3+}$	(*b*) sp^3
(*iii*) Boron in B_2H_6	(*c*) sp^3d^2
(*iv*) Carbon in Buckminster fullerene	
(*v*) Silicon in SiO_4^{4-}	
(*vi*) Germanium in $[GeCl_6]^{2-}$	

Answers

22. (*i*) – (*e*); (*ii*) – (*c*); (*iii*) – (*d*); (*iv*) – (*a*, *b*) **23.** (*i*) – (*c*); (*ii*) – (*d*); (*iii*) – (*a*); (*iv*) – (*e*); (*v*) – (*b*)
24. (*i*) – (*b*); (*ii*) – (*c*); (*iii*) – (*b*); (*iv*) – (*a*); (*v*) – (*b*); (*vi*) – (*c*)

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Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

(*a*) Both A and R are correct and R is the correct explanation of A.

(*b*) Both A and R are correct but R is not the correct explanation of A.

(*c*) Both A and R are not correct.

(*d*) A is not correct but R is correct.

25. Assertion (A) : If aluminium atoms replace a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires a negative charge.
Reason (R) : Aluminium is trivalent while silicon is tetravalent.

26. Assertion (A) : Silicones are water repelling in nature.
Reason (R) : Silicones are organosilicon polymers, which have $(-R_2SiO-)$ as repeating unit.

Answers

25. (*a*) **26.** (*b*)

Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A1.(*a*) : $Na_2B_4O_7 + 2H_2O \longrightarrow \underset{\text{alkaline}}{H_2B_4O_7} + 2NaOH$

A2. (*c*) : $H_3BO_3 \xrightarrow{373\,K} HBO_2 \xrightarrow[\text{hot}]{\text{Red.}} \underset{\text{Boron trioxide}}{B_2O_3}$

A5. (*b*) : Diborane (B_2H_6) contains two three centre two electron bonds (B–H–B).

A11.(*c*) : $B_2H_6 + 6H_2O \longrightarrow \underset{\text{acidic}}{2H_3BO_3} + 6H_2$

A15. (*c*) : $\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \xrightarrow{\text{Heat}} 2CaCO_3 + \underset{\text{Borax}}{Na_2B_4O_7} + 2NaBO_2$

A19.(*a*) : $Na_2B_4O_7 + 7H_2O \longrightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$

A20.(*b*) : $Al_2O_3 + 3C + 3Cl_2 \longrightarrow \underset{\text{anhyd.}}{2AlCl_3} + 3CO\uparrow$

B. *mcq from competitive examinations*

B9(*c*) : When diborane is hydrolysed, it forms orthoboric acid and hydrogen.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

B10.(*d*) : The basic structural unit of silicates is SiO_4^{4-}.

B11.(*a*) : It can only form dimer.

B12.(*b*) : Diborane, B_2H_6 has three centred two electron bond.

B14.(*b*) : PF_3 has a lone pair of electrons. Therefore, it is most likely to behave as Lewis base.

B16.(*d*) : Because of inability of ns^2 electrons of the valence shell to participate in bonding on moving down the group (inert pair effect).

Pb (II) is more stable than Pb (IV) and

Sn (IV) is more stable than Sn (II)

Therefore, Pb (IV) is easily reduced to Pb (II) and hence Pb (IV) is oxidising agent.

Sn (II) is easily oxidised to Sn (IV) and hence Sn (II) is reducing agent.

B17.(*c*) : Boron cannot form MF_6^{3-} because of the absence of *d*-orbitals in its valence shell.

B18.(*d*) : In group 13, atomic radii increases down the group but Ga has smaller atomic radius than Al. Therefore, correct order is

$$B < Ga < Al < In < Tl$$

B22. (*b*) : Aluminium chloride in aqueous solution exists as ion pair

$$AlCl_3 + 6H_2O \rightleftharpoons [AlCl_2(H_2O)_4]^+(aq) + [AlCl_4(H_2O)_4]^-$$

The crystallisation of aqueous $AlCl_3$ gives an ionic solid $[AlCl_2(H_2O)_4]^+$, $[AlCl_2(H_2O)_2]^-$ which on further heating gives Al_2Cl_6.

$$[AlCl_2(H_2O)_4]^+[AlCl_4(H_2O)_2]^- \xrightarrow{\text{Heat}} Al_2Cl_6 + 2H_2O$$

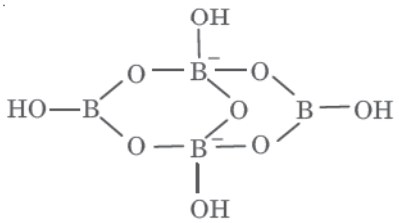
B27.(*b*) : The stability of lower oxidation state increases down the group as

$$SiX_2 < < GeX_2 < < SnX_2 < < PbX_2$$

B44.(*c*) : Ionic character is inversely proportional to the polarising power of the cation. The polarising power decreases with increase in size of cation *i.e.*, $B^{3+} > Ga^{3+} > Al^{3+}$. Therefore, BCl_3 will have the least ionic character and $AlCl_3$ will have the maximum ionic character. The correct order is:

$$AlCl_3 > GaCl_3 > BCl_3$$

B45.(*a*) : The structure of borax ion is



B — O — B links = 5, B — OH links = 4

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Competition File

B47.(*a*) : Metallic character increases down the group and decreases along a period.

B < Al, Mg < K, Mg > Al

The correct order B < Al < Mg < K

B50.(*a*) : Lewis acid strength decreases down the group.

B52.(*d*) : Orthoboric acid is formed when an aqueous solution of borax is treated with mineral acids; hydrochloric acid or sulphuric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$
$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$$

B54.(*b*) : Aluminium sulphate is mainly used as a coagulating agent in purification of drinking water and in waste water treatment plants, as mordant in dyeing and printing textile and also used in calico printing and in paper industry.

B56.(*d*) : Silicon has vacant *d*-orbitals in its valence shell while carbon has only *s*- and *p*-orbitals. Therefore, carbon cannot increase its coordination number beyond 4 while silicon can. Therefore, $SiCl_4$ can be readily hydrolysed by water by extending its octet.

B57.(*b*) : BaO (basic), Al_2O_3(amphoteric), SO_2(acidic)

B58.(*c*) : $Al + 3H_2O \xrightarrow{NaOH} \underset{\text{White gelatinous ppt (X)}}{Al(OH)_3}$

X is soluble in excess NaOH

$$Al(OH)_3 \xrightarrow{\text{excess NaOH}} \underset{\text{Sodium meta aluminate}}{NaAlO_2}$$

$$2Al(OH)_3 \xrightarrow[\text{heating}]{\text{Strong}} Al_2O_3$$

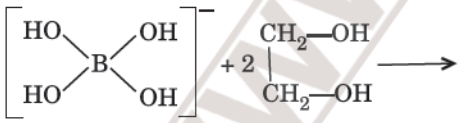
Al_2O_3 is used in column chromatography.

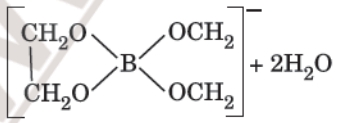
B60.(*d*) : Al has similar electronegativity to Be (diagonal relationship)

B62.(*d*) : In B_2H_6, there are four 2-centre-2-electron (B–H) bonds and two 3-centre-2-electron (B–H–B) bonds.

B63.(*d*) : CCl_4 cannot get hydrolysed due to the absence of *d*-orbitals in the valence shell of carbon.

B64.(*a*) :





Due to the formation of Lewis acid-base complex ion, the equilibrium shifts in the forward direction.

B65.(*a*) : $H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

B66.(*c*) : $Al(OH)_3$ forms gelatinous mass.

B67.(*b*) : The atomic radius of Ga is less than Al due to the presence of *d*-orbitals in gallium. *d*-orbitals have a poor shielding effect as a result of which size decreases.

C. *mcq with more than one correct answer*

C7.(*b, d*). Orthoboric acid (H_3BO_3) behaves as a weak mono basic acid (Lewis acid). It accepts a pair of lone pair from OH^- ion.

$H—OH + B(OH)_3 \longrightarrow [B(OH)_4]^- + H^+$

On adding ethylene glycol, its acidity increases.

C11. (*a, b, c*).

(*a*) $Al(CH_3)_3$ has two 3-centre 2-electron bonds in its $Al_2(CH_3)_6$ structure.

(*b*) BH_3 has two 3-centre 2-electron bonds in its B_2H_6 structure.

(*c*) BCl_3 is stronger Lewis acid because of small size of B.

(*d*) Al_2Cl_6 does not have 3-centre 2-electron bonds.

NCERT Exemplar Problems: MCQs Type I

2. (*a*) $AlCl_3$ is a Lewis acid because it is electron deficient.

5. (*a*) Boron cannot form BF_6^{3-} because it has no outer *d*-orbitals and hence cannot extend the octet.

6. (*c*) $B(OH)_3 + H—OH \longrightarrow [B(OH)_4]^- + H^+$

Boric acid

or $B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$

7. (*b*) Catenation decreases rapidly as the strength of element-element bond decreases due to increasing size down the group i.e., C >> Si > Ge ≈ Sn.

8. (*c*) Chain of silicon polymer can be controlled by adding $(CH_3)_3$ SiCl.

11. (*a*) $\underset{\text{Diborane (X)}}{B_2H_6} + 6NH_3 \xrightarrow{450K} \underset{\text{Inorganic benzene}}{2B_3N_3H_6} + 12H_2$

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

12. (*b*) Quartz is made up of silicon.

13. (*d*) $SnCl_2$ can be easily oxidised to Sn^{4+} because +4 oxidation state of Sn is more stable than +2 oxidation state.

14. (*c*) Solid CO_2 is known as dry ice.

15. (*b*) : Cement contains elements of group 2 (Ca), group 13 (Al) and group 14 (Si).

NCERT Exemplar Problems: MCQs Type II

16. (*a, b*) Poor shielding of *d*-electron increases nuclear charge.

17. (*b, c*) The linear shape of CO_2 is due to *sp* hybridisation of carbon and $p\pi$–$p\pi$ bonding between carbon and oxygen.

18. (*a, b*) Me_3 SiCl is used to control the length of silicone polymers by blocking the end terminal of the silicone polymer.

21. (*b, d*) CO_2 is a resonance hybrid of the following structures :

$O = C = O \leftrightarrow {}^+O \equiv C - O^- \leftrightarrow {}^-O - C \equiv O^+$

NCERT Exemplar Problems: Assertion-Reason Type

26. (*b*) : Correct explanation : Silicon atoms in silicones are surrounded by non-polar alkyl groups which repel water molecules.

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Unit Practice Test

for Board Examination

Time Allowed: 1 Hr. ***Maximum Marks: 25***

1. Which out of $SiCl_4$ and CCl_4 gets easily hydrolysed? (1)

2. $PbCl_2$ is more stable than $PbCl_4$. Why? (1)

3. What is maximum covalency of silicon in its compounds? (1)

4. Write resonating structures of CO_2. (1)

5. Is boric acid a protic acid? (1)

6. Suggest a reason why the B–F bond length in BF_3 (130 pm) and BF_4^- (143 pm) differ. (2)

7. Why does BF_3 behave as Lewis acid? (2)

8. How would you explain the lower atomic radius of gallium as compared to aluminium ? (2)

9. Explain

(*i*) SiF_6^{2-} is known but CF_6^{2-} is not formed.

(*ii*) $(CH_3)_3N$ is basic but $(CF_3)_3N$ is not basic.

(*iii*) Although diamond is covalent but it has very high melting point. (3)

10. When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities. (3)

11. Complete the following reactions :

(*i*) $BCl_3 + H_2O \longrightarrow$

(*ii*) $SiF_4 + HF \longrightarrow$

(*iii*) $ZnO + CO \longrightarrow$

(*iv*) $Al_2O_3.\ 2H_2O + NaOH + H_2O \longrightarrow$

(*v*) $Pb + NaOH + H_2O \longrightarrow$

(*vi*) $NaH + B_2H_6 \longrightarrow$ (3)

12. (*a*) Account for the fact that aluminium chloride exists as dimer.

(*b*) Give different products formed when diborane reacts with ammonia.

(*c*) What are silicones? Explain. (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part II of the book.

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UNIT 11A

p-BLOCK ELEMENTS

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GROUP 15 ELEMENTS

Group 15 of the periodic table contains five elements namely *nitrogen* (N), *phosphorus* (P), *arsenic* (As), *antimony* (Sb) and *bismuth* (Bi). This group is regarded as **nitrogen family**. Collectively, the group 15 elements are also called **pnicogens** and their compounds as **pniconides**. The name is derived from the Greek word *pnicomigs* meaning *suffocation*.

OCCURRENCE

The elements of group 15, except phosphorus do not occur very abundantly in nature. Though **molecular nitrogen** comprises about 78% by volume of the earth's atmosphere, it is not very abundant in the earth's crust. It is only **thirty third** most abundant element by weight in the earth's crust. Since nitrates are very soluble in water so these are not widespread in the earth's crust. The only major nitrate minerals are $NaNO_3$ (*sodanitre, Chile saltpetre*) and KNO_3 (*nitre, Indian saltpetre*). The major deposits of saltpetre (KNO_3) occur in India. Nitrogen is also an important constituent of proteins, amino acids and nucleic acids in plants and animals. The continuous interchange of nitrogen between the atmosphere and biosphere is called **nitrogen cycle**.

Phosphorus is the **eleventh** element in order of abundance in crustal rocks of the earth. It is very reactive element and therefore it does not occur in free state in nature. All its known minerals are orthophosphates. Major amounts of phosphorus occur in a single mineral family known as **apatites**, which have the general formula, $3Ca_3(PO_4)_2\ CaX_2$ or $Ca_9(PO_4)_6.CaX_2$ or $Ca_{10}(PO_4)_6X_2$ where X = F, Cl or OH. The common minerals of phosphorus are:

(*i*) *Phosphorite* : $Ca_3(PO_4)_2$

(*ii*) *Fluorapatite* : $Ca_5(PO_4)_3F$

or $3Ca_3(PO_4)_2.CaF_2$

(*iii*) *Chlorapatite* : $Ca_5(PO_4)_3Cl$

or $3Ca_3(PO_4)_2.CaCl_2$

(*iv*) *Hydroxyapatite* : $Ca_5(PO_4)_3OH$

or $3Ca_3(PO_4)_2.Ca(OH)_2$

Large deposits of phosphate rocks are located in North Africa and North America. In India, the phosphate rocks are mainly found in Rajasthan.

Phosphorus is essential for life, as a structural material in both animals and plants. It is present in bones as well as in living cells. About 60% bones and teeth are $Ca_3(PO_4)_2$ or $[3\{Ca_3(PO_4)_2\}.CaF_2]$. It also occurs in nucleic acids (DNA and RNA) which control the hereditary effects in human beings. Phosphorus is also found in ATP (adenosine triphosphate) and ADP (adenosine diphosphate) which are of vital importance for production of energy in the cells. Phospho proteins are present in eggs and milk.

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The elements **arsenic**, **antimony and bismuth** are not very abundant. Their important sources are sulphides occurring as traces in other ores *e.g.*, arsenopyrites, FeAsS; stibnite, Sb_2S_3, bismuth glance, Bi_2S_3. These are obtained as metallurgical by-products from roasting sulphide ores.

GENERAL CHARACTERISTICS OF GROUP 15 ELEMENTS

A. Electronic Configurations

The atoms of group 15 have five electrons in the outermost shell, two in *s* and three in *p* subshell. The general electronic configuration of this group may be expressed as ns^2np^3.

Table 1. Electronic configuration of group 15 elements.

Element	Symbol	Atomic No.	Electronic configuration
Nitrogen	N	7	[He] $2s^2 2p^3$
Phosphorus	P	15	[Ne] $3s^2 3p^3$
Arsenic	As	33	[Ar] $3d^{10} 4s^2 4p^3$
Antimony	Sb	51	[Kr] $4d^{10} 5s^2 5p^3$
Bismuth	Bi	83	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$

B. Atomic and Physical Properties

The important atomic and physical properties of group 15 elements are given in Table 2.

Table 2. Some important atomic and physical properties of group 15 elements.

		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic mass (g mol^{-1})		14.01	30.97	74.92	121.75	208.96
Atomic radius covalent (pm)		70	110	121	141	148
Ionic radius (pm)		171 (N^{3-})	212 (P^{3-})	222 (As^{3-})	76 (Sb^{3+})	103 (Bi^{3+})
Ionisation enthalpy (kJ mol^{-1})	IE_1	1402	1012	947	834	703
	IE_2	2856	1903	1798	1595	1610
	IE_3	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9
m.p. (K)		63 (Molecular)	317.1 (White P)	1089 (Grey α-form at 38.6 atm)	904	544.4
b.p. (K)		77.2 (Molecular)	553.5 (White P)	888 (Sublimation temp.)	1860	1837
Density (g cm^{-3}) at 298 K		0.879 (at 63 K)	1.823	5.778 (Grey α-form)	6.697	9.808

The important trends of atomic and physical properties are discussed below:

1. Atomic and ionic radii. *The atomic and ionic radii of group 15 elements are smaller than the atomic radii of the corresponding group 14 elements.* On going down the group, *the atomic radii increase with increase in atomic number.*

Explanation. The nuclear charge in case of elements of group 15 is larger than in the case of elements of group 14. Due to increased nuclear charge, the electrons are strongly attracted by the nucleus and therefore, atomic radii decrease. Thus, the atomic radii of elements of group 15 are less than those of group 14.

On moving down the group, the atomic radii increase due to increase in number of shells because of addition of a new principal shell in each succeeding element. However, from As to Bi, only a small increase in covalent radius is observed. This is due to the presence of completely filled *d*- and or *f*-orbitals in the heavier members.

2. Ionisation enthalpies. *The first ionisation enthalpies of the group15 elements are higher than the corresponding members of the group 14 elements.* On going down the group, *the ionisation enthalpies decrease.*

Explanation. The larger ionisation enthalpy is due to greater nuclearcharge, small size and stable configuration of the atoms of group 15 elements. The electronic configuration of atoms of group 15 are half filled, np_x^1, np_y^1, np_z^1 and are stable. Therefore, they have high ionisation enthalpies.

The decrease in ionisation enthalpy, as we move down the group, is due to increase in atomic size and screening effect which overweigh the effect ofincreased nuclear charge.

As expected, the successive ionisation enthalpies of these elements (Table 2) increase in the order :

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$$

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3. Electronegativity. *The electronegativity values of elements of group 15 are higher than the corresponding elements of group 14. On going down the group, the electronegativity value decreases.*

Explanation. The elements of group 15 have smaller size and greater nuclear charge of atoms and therefore, they have higher electronegativity values.

The decrease in electronegativity on going down the group is due to increase in size of the atoms and shielding effect of inner electron shells on going down the group. However, amongst the heavier elements, the difference is not that much pronounced.

4. Metallic character. *The elements of group 15 are less metallic.* However, on going down the group, *the metallic character increases from N to Bi.* For example, N and P are non-metallic, As and Sb are partly non-metallic while Bi is a metal.

N — P (Non-metals) | As — Sb (Metalloids) | Bi (Metal)

Metallic character increases →

Explanation. Due to increased nuclear charge and higher electronegativity, the elements of group 15 are less metallic than the corresponding elements of group 14. On moving down the group, the atomic size as well as the screening effect of the intervening electrons increases. As a result, the ionization enthalpy decreases and therefore, metallic character increases down the group.

5. Melting and boiling points. *The melting points of group 15 elements first increase from nitrogen to arsenic and then decrease to antimony and bismuth. However, the boiling points increase regularly on going from nitrogen to bismuth.*

Explanation. The melting points increase down the group due to increase in atomic size. However, the unexpected decrease in the melting points of Sb and Bi is because of their tendency to form three covalent bonds instead of five covalent bonds, due to **inert pair effect**. As a result, the attraction among their atoms is weak and hence their melting points are low. Because of large size of atoms, Bi has still weaker interatomic forces than Sb and therefore, has still lower melting point.

The boiling points increase down the group from N to Bi because of increase in their atomic size.

6. Catenation. *The elements of group 15 also show a tendency to form bonds with itself (self linking of atoms) known as* **catenation**. All these elements show this property but to a much smaller extent than carbon. For example, hydrazine (H_2NNH_2) has two N atoms bonded together, hydrazoic acid (N_3H) has three N-atoms, azide ion, N_3^- has also three N atoms bonded together

Hydrazoic acid, HN_3 : $H—\ddot{N}=\overset{+}{N}=\ddot{N}:^-$

Azide ion, N_3^- : $:\ddot{N}=\overset{+}{N}=\ddot{N}:^-$

Among the elements of group 15, phosphorus has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorus atoms.

Diphosphine (P_2H_4) has two phosphorus atoms bonded together.

The lesser tendency of elements of group 15 to show catenation in comparison to carbon is their low (M—M) bond dissociation enthalpies.

Bond	C—C	N—N	P—P	As—As
Bond energy (kJ mol ^{1})	353.3	163.8	201.6	147.4

REMEMBER

- The element having maximum tendency for catenation in the periodic table is **carbon**.
- Among the elements of group 15, P has maximum tendency for catenation.

7. Allotropy. Except nitrogen and bismuth, all other elements of this group show allotropy. For example,

phosphorus exists as : white, black or red phosphorus

arsenic exists as : yellow or grey arsenic

antimony exists as : yellow or silvery grey allotropic forms.

C. Oxidation States

The elements of group 15 have five electrons in their valence shell. They exhibit various oxidation states from –3 to +5 as discussed below :

(*i*) Negative oxidation states. These elements have five electrons in the valence shell *(ns^2np^3)* and therefore, require three more electrons to acquire the nearest noble gas configuration. But, the gain of three electrons is not energetically favourable because it requires very large amount of energy to gain three electrons and form M^{3-} ions. However, nitrogen being the smallest and most electronegative element of the group forms N^{3-} (nitride) ion and shows an oxidation state of – 3 in nitrides of some highly electropositive metals such as Mg_3N_2, Ca_3N_2, etc. The other elements of this group form covalent compounds even with metals and show an oxidation state of –3 with metals. For example, calcium phosphide (Ca_3P_2), sodium arsenide (Na_3As), zinc antimonide (Zn_3Sb_2), magnesium bismuthide (Mg_3Bi_2). As is evident from the decreasing electronegativities and decreasing ionisation enthalpies, **the tendency of the elements to exhibit –3 oxidation state decreases on moving down from P to Bi** due to increase in size and metallic character.

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In fact, the last member of the group, Bi hardly forms any compound in –3 oxidation state.

In addition to –3 oxidation state, N and P show oxidation states of –2 in hydrazine (NH_2NH_2) and diphosphine (P_2H_4) respectively. Nitrogen also shows an oxidation state of –1 in hydroxyl amine (NH_2OH) but P does not.

(*ii*) **Positive oxidation states.** All the elements of group 15 also exhibit positive oxidation states of +3 and +5. However, **on moving down the group, the stability of +5 oxidation state decreases while that of +3 oxidation state increases due to inert pair effect**.

Because of energy considerations, these elements cannot lose all the five valence electrons. Therefore, they do not form M^{5+} ions and all the compounds of group 15 elements having +5 oxidation state (*i.e.,* PF_5, PCl_5, SbF_5, BiF_5, etc.) are essentially covalent compounds.

Nitrogen does not form compounds in +5 oxidation state such as NF_5, NCl_5, etc., because it does not have vacant *d*-orbitals in its valence shell which can enable it to extend its octet. The stability of the highest oxidation state (+5) decreases down the group. For example, the +5 oxidation state of Bi is less stable than that of Sb. This is due to inert pair effect. The only well characterised Bi(V) compound is BiF_5.

The elements of group 15 form both covalent (*e.g.,* NCl_3, PCl_3 $AsCl_3$, $SbCl_3$) and ionic compounds (*e.g.,* BiF_3, SbF_3, etc.) in +3 oxidation state. The +3 oxidation state becomes more and more stable on moving down the group.

Nitrogen and phosphorus also show oxidation state of +4 because of the ability of one lone pair on NH_3 and PH_3 to form dative bonds with Lewis acids. However, nitrogen can exist in various oxidation states from –3 to +5 in its hydrides, oxides and oxoacids as shown below :

Compound	NH_3 Ammonia	N_2H_4 Hydrazine	NH_2OH Hydroxyl amine	N_2 Nitrogen	N_2O Nitrous oxide	NO Nitric oxide	N_2O_3 Nitrogen trioxide	N_2O_4 Nitrogen tetraoxide	N_2O_5 Nitrogen pentaoxide
Oxidation state	–3	–2	–1	0	+1	+2	+3	+4	+5

Phosphorus also exhibits +1 and +4 oxidation states in some oxoacids.

(*iii*) **Disproportionation :** In case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

$$\overset{+3}{3HNO_2} \longrightarrow \underset{\text{Nitrous acid}}{\overset{+5}{HNO_3}} + \underset{\text{Nitric acid}}{\overset{+2}{2NO}} + H_2O$$

Nitric oxide

Similarly, in case of P nearly all the intermediate oxidation states disproportionate into +5 and –3 both in acid and alkali solutions. For example,

$$\underset{\text{Phosphorous acid}}{\overset{+3}{4H_3PO_3}} \longrightarrow \underset{\text{Phosphoric acid}}{\overset{+5}{3H_3PO_4}} + \underset{\text{Phosphine}}{\overset{-3}{PH_3}}$$

However, +3 oxidation state in As, Sb and Bi becomes increasingly stable with respect to disproportionation because of inert pair effect. Therefore, their tendency to undergo disproportionation decreases.

(*iv*) **Maximum covalency : The maximum covalency of nitrogen is restricted to four because** it does not have vacant *d*-orbitals in its outermost valence shell (n = 2). Therefore, only four (one 2*s* and three 2*p*) orbitals are available for bonding and it cannot extend its valency beyond four (*e.g.,* $(NH_4^+$, $(CH_3)_4N^+$, etc.). That is the reason why nitrogen does not form pentahalides such as NF_5 or NCl_5. On the other hand, phosphorus and all other elements have vacant *d*-orbitals in their valence shells and can use all their valence orbitals to exhibit covalency of five or six *e.g.,* PF_5, PCl_5, AsF_5, PF_6^-, $[SbF_6]^-$, etc.

REMEMBER

- In the last element of a group, after the removal of electrons from *p*-orbitals, the remaining ns^2 (*e.g.* $6s^2$) electrons behave like stable noble gas and donot take part in compound formation. *This reluctance of the s-electron pair to take part in chemical combination* is called **inert pair effect**.
- **NCl_5 and NF_5 donot exist.**
  Nitrogen does not form compounds in +5 oxidation state such as NCl_5, NF_5 , etc. because of the absence of *d*-orbitals in its valence shell.

CHEMICAL PROPERTIES AND TRENDS IN CHEMICAL REACTIVITY

Like first member of other groups, nitrogen differs from rest of members of the group due to its (*i*) smaller size, (*ii*) high electronegativity, (*iii*) high ionisation enthalpy and (*iv*) non-availability of *d*-orbitals in the valence shell.

Nitrogen has unique tendency to form $p\pi$–$p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (*e.g.,* C and O). However, the heavier elements of this group do not form $p\pi$–$p\pi$ bonds because their atomic orbitals are so large and diffused that they cannot have effective overlapping. These differences between nitrogen and other members of the group result into **anomalous properties of nitrogen** as explained below :

- Nitrogen is a colourless gas and exists as a diatomic molecule. The two nitrogen atoms are held together

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by a triple bond (one σ and two π) between two atoms and have very high bond enthalpy (941.4 kJ mol^{-1}).

:N ⋮⋮ N: or :N≡≡N:

Nitrogen molecule is inert and has very low reactivity because it has triple bond and therefore, has very high bond enthalpy (941.4 kJ mol^{-1}).

Due to the presence of triple bond, which has very high bond enthalpy, the nitrogen molecule is inert and has very low reactivity. However, the tendency to form multiple bonds ($p\pi$–$p\pi$) is limited only to nitrogen. On the other hand, phosphorus, arsenic and antimony exist in various forms containing single bonds as P—P, As—As and Sb—Sb. For example, phosphorus exists as tetrahedral P_4 molecules as shown in Fig. 1.

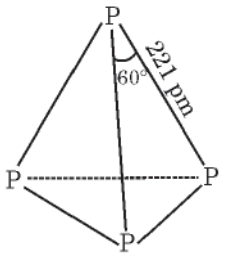

Fig. 1. Structure of P_4 molecule.

In this case, four P atoms lie at the corners of a regular tetrahedron. Each P is bonded to three P atoms by single P—P bonds. However, the single N—N bond is weaker than the single P—P bond because of high interelectronic repulsions of non bonding electrons due to small bond length (109 pm). As a result, the catenation tendency is weaker in nitrogen. Therefore, **nitrogen exists as gas while phosphorus exists as solid.**

- Since P—P single bond is much weaker than N≡≡N triple bond, therefore, phosphorus is much more reactive than nitrogen. For example, white phosphorus is more reactive than nitrogen. It catches fire when exposed to air and burns to form the oxide, P_4O_{10}. It is stored under water to prevent it from burning. Red P is stable in air at room temperature but reacts on heating.

The reactivity of other elements **decreases from As to Bi**. Arsenic and antimony both occur in two forms. The most reactive is yellow form which contains M_4 tetrahedral units and resembles white phosphorus. Arsenic is stable in dry air but tarnishes in moist air giving first a bronze and then a black coating on its surface.

Antimony is less reactive and is stable towards water and air at room temperature. On heating in air, it forms Sb_4O_6, Sb_4O_8 or Sb_4O_{10}. Bismuth forms Bi_2O_3 on heating.

Another factor which affects the chemistry of nitrogen is the absence of *d*-orbitals in its valence shell. **Nitrogen cannot form $p\pi$—$d\pi$ bonds** whereas phosphorus and other heavier members of this group readily form $p\pi$—$d\pi$ multiple bonds. For example, phosphorus forms compounds containing $p\pi$—$d\pi$ bonds such as $R_3P = O$, $R_3P = CH_2$ (R = alkyl group), POX_3 (X = F, Cl, Br), etc. Phosphorus and arsenic can also form $d\pi$—$d\pi$ bonds with transition metals where their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands. Recently, a few stable compounds of P, As and Sb containing $p\pi$—$p\pi$ bonds *(e.g.,* P = C, P = N, P = P, As = As, etc.) have been synthesized.

Let us discuss some trends in chemical reactivity of group 15 elements and their compounds.

1. Reactivity towards hydrogen (formation of hydrides)

All the elements of group 15 form gaseous trihydrides of the formula EH_3 (where E = N, P, As, Sb or Bi) such as :

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Ammonia	Phosphine	Arsine	Stibine	Bismuthine

The lighter elements also form hydrides of the formula M_2H_4 such as N_2H_4 (hydrazine), P_2H_4 (diphosphine) and As_2H_4 (diarsine). Nitrogen also forms a special hydride of the formula HN_3, known as hydrogen azide or hydrazoic acid.

Nitrogen forms a special hydride:
HN_3 : **hydrogen azide or hydrazoic acid**

Preparation. (*i*) By hydrolysis of binary metal compounds. The trihydrides can be easily obtained by the hydrolysis of their binary metal compounds with water or dilute acids :

$$\underset{\text{Magnesium nitride}}{Mg_3N_2} + 6H_2O \longrightarrow 3Mg(OH)_2 + \underset{\text{Ammonia}}{2NH_3}$$

$$\underset{\text{Calcium nitride}}{Ca_3N_2} + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

$$\underset{\text{Calcium phosphide}}{Ca_3P_2} + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{\text{Phosphine}}{2PH_3}$$

$$\underset{\text{Zinc arsenide}}{Zn_3As_2} + 6HCl \longrightarrow 3ZnCl_2 + \underset{\text{Arsine}}{2AsH_3}$$

$$\underset{\text{Magnesium bismuthide}}{Mg_3Bi_2} + 6HCl \longrightarrow 3MgCl_2 + \underset{\text{Bismuthine}}{2BiH_3}$$

***(ii)* By reduction of trichlorides.** The trichlorides of these elements except that of bismuth give the corresponding hydrides on reduction with Zn/acid or $LiAlH_4$.

$$ECl_3 + 3LiAlH_4 \longrightarrow EH_3 + 3LiCl + 3AlH_3$$

(E = N, P, As, Sb)

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Structure. All these hydrides are covalent in nature and have *pyramidal structure.* These involve sp^3 hybridization of the central atom and one of the tetrahedral position is occupied by a lone pair. The structure of NH_3 molecule is shown in Fig. 2.

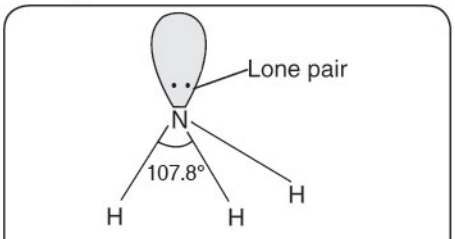

Fig. 2. Shape of NH_3 molecule.

Due to the presence of lone pair, the bond angle in NH_3 is less than the normal tetrahedral angle. It has been found to be 107.8°. As we go down the group the **bond angle decreases as**:

NH_3	PH_3	AsH_3	SbH_3	BiH_3
107.8°	93.6°	91.8°	91.3°	90°

Explanation. In all these hydrides, the central atom is surrounded by four electron pairs, three bond pairs and one lone pair. Now, as we move down the group from N to Bi, the size of the atom goes on increasing and its electronegativity decreases. Consequently, the position of bond pair shifts more and more away from the central atom in moving from NH_3 to BiH_3. For example, the bond pair in NH_3 is close to N in N—H bond than the bond pair in P—H bond in PH_3. As a result, the force of repulsion between the bonded pair of electrons in NH_3 is more than in PH_3. In general, the force of repulsion between bonded pairs of electrons decreases as we move from NH_3 to BiH_3 and therefore, the bond angle also decreases in the same order.

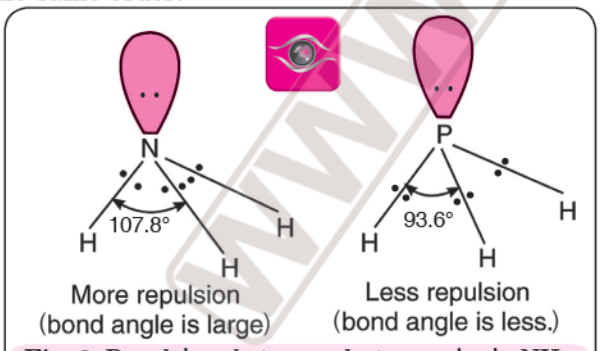

Fig. 3. Repulsions between electron pairs in NH_3 and PH_3.

Characteristics of hydrides. The important characteristics of these hydrides are :

(*i*) Basic strength. All these hydrides have one lone pair of electrons on their central atom. Therefore, *they act as Lewis bases.* They can donate an electron pair to electron deficient species (Lewis acids). **As we go down the group, the basic character of these hydrides decreases.** For example, NH_3 is distinctly basic; PH_3 is weakly basic; AsH_3, SbH_3 and BiH_3 are very weakly basic.

Explanation. Nitrogen atom has the smallest size among the hydrides. Therefore, the lone pair is concentrated on a small region and electron density on it is the maximum. Consequently, its electron releasing tendency is maximum. As the size of the central atom increases down the family, the electron density also decreases. As a result, the electron donor capacity or the basic strength decreases down the group.

(*ii*) Thermal stability. *Thermal stability of the hydrides of group 15 elements decreases as we go down the group.* Therefore, NH_3 is most stable and BiH_3 is least stable. The stability of the hydrides of group 15 elements decreases in the order :

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

Explanation. This is due to the fact that on going down the group, the size of the central atom increases and therefore, its tendency to form stable covalent bond with small hydrogen atom decreases. As a result the M—H bond strength decreases and therefore thermal stability decreases.

(*iii*) Reducing character. *The reducing character of the hydrides of group 15 elements increases from NH_3 to BiH_3.* Thus, increasing order of reducing character is as follows :

$$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$

Explanation. The reducing character depends upon the stability of the hydride. The lesser the stability of a hydride, the greater is its reducing character. Since the stability of group 15 hydrides decreases from NH_3 to BiH_3, hence the reducing character increases. For example, NH_3 being most stable among the group 15 hydrides is not a good reducing agent. The other hydrides being unstable act as good reducing agents. However, it may be noted that ammonia at high temperatures reduces copper oxide to copper :

$$3CuO + 2NH_3 \xrightarrow{\text{heat}} 3Cu + N_2 + 3H_2O$$

(*iv*) Boiling and melting points. *Ammonia has a higher boiling point than phosphine and then the boiling point increases down the group because of increase in size.(Fig. 4).*

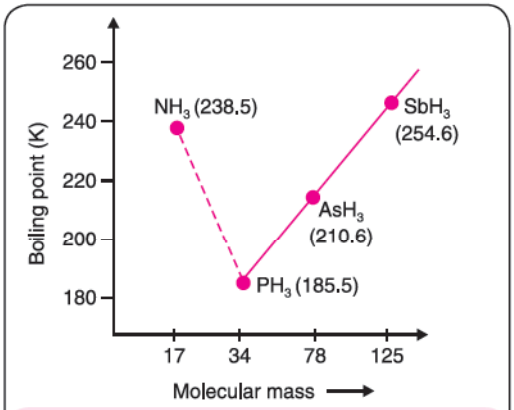

Fig. 4. Plot of boiling points of the hydrides of group 15 elements.

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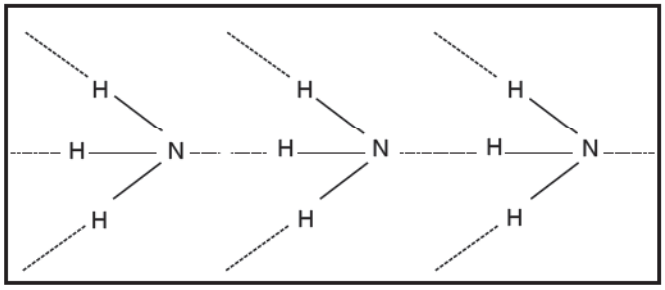
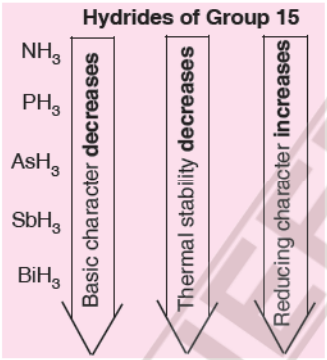
Molecule	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Boiling point (K)	238.5	185.5	210.6	254.6	290
Melting point (K)	195.2	139.5	156.7	185.0	—

Similar behaviour is observed for melting points.

Explanation. The abnormally high boiling point of ammonia is due to its *tendency to form hydrogen bonds*. The electronegativity of N (3.0) is much higher than that of H (2.1). As a result N–H bonds are polar and therefore, NH_3 undergoes intermolecular hydrogen bonding as shown below:



In PH_3 and other hydrides, the intermolecular forces are van der Waals forces. These van der Waals forces increase with increase in molecular size and therefore, boiling points increase on moving from PH_3 to BiH_3.



(*v*) Solubility. Ammonia forms hydrogen bonding with water molecules while phosphine and other hydrides do not form hydrogen bonding with water. Therefore, NH_3 is soluble in water while PH_3 and other hydrides are insoluble in water.

The trends in the properties of hydrides of group 15 are given in Table 3.

Table 3. Properties of hydrides of group 15 elements.

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point (K)	195.2	139.5	156.7	185	–
Boiling point (K)	238.5	185.5	210.6	254.6	290
(E – H) distance (pm)	101.7	141.9	151.9	170.7	–
HEH angle (°)	107.8	93.6	91.8	91.3	–
$\Delta_f H°$ (kJ mol^{-1})	– 46.1	13.4	66.4	145.1	278
$\Delta_{diss} H°$(E–H) (kJ mol^{-1})	389	322	247	255	–

2. Reactivity towards oxygen (formation of oxides)

The elements of group 15 combine with oxygen directly or indirectly to form two types of oxides, E_2O_3 (trioxides) and E_2O_5 (pentaoxides). However, nitrogen forms a number of oxides with oxidation states ranging from +1 to +5 which have no analogues of P, As, Sb or Bi. This is mainly because of strong tendency of nitrogen to form $p\pi$—$p\pi$ multiple bonds with oxygen. The important oxides of group 15 elements along with their oxidation states are listed in Table 4.

Table 4. Oxides of group 15 elements in different oxidation states.

Element ⟶ Oxidation state	N	P	As	Sb	Bi
+1	N_2O Nitrous oxide				
+2	NO Nitric oxide				
+3	N_2O_3 Dinitrogen trioxide	P_4O_6 Phosphorus trioxide	As_2O_3 Arsenic trioxide	Sb_2O_3 Antimony trioxide	Bi_2O_3 Bismuth trioxide
+4	N_2O_4 Dinitrogen tetraoxide	P_4O_8 Phosphorus tetraoxide			
+5	N_2O_5 Dinitrogen pentoxide	P_4O_{10} Phosphorus pentoxide	As_2O_5 Arsenic pentoxide	Sb_2O_5 Antimony pentoxide	Bi_2O_5 Bismuth pentoxide
	ACIDIC CHARACTER DECREASES ⟶				

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There is an important difference between the oxides of nitrogen and other group congeners in their structures. ***The nitrogen has ability to form pπ–pπ multiple bonds and this is present in its structures.***

On the other hand, the reluctance of P, As, Sb and Bi to form $p\pi$–$p\pi$ multiple bonds leads to the cage structures for their oxides.

The oxides in the higher oxidation state of the elements are more acidic than that of the oxides in the lower oxidation state. The acidic character of the oxides of group 15 elements decreases down the group. All the oxides of nitrogen except N_2O and NO and phosphorus are strongly acidic; oxides of arsenic are weakly acidic; oxides of antimony are amphoteric while those of bismuth are weakly basic.

The basic nature of oxides increases with increasing atomic number. For example, P (III) and As (III) oxides are acidic, Sb (III) oxide S amphoteric and Bi (III) oxide is distinctly basic. It dissolves in acids to form salts.

$$Bi_2O_3 + 6HNO_3 \longrightarrow 2Bi(NO_3)_3 + 3H_2O$$

Acidic character of oxides of elements of group 15

- $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$ (N_2O & NO are neutral)
- $N_2O_3 > P_4O_6 > As_4O_6 > Sb_4O_6$ (As_4O_6 & Sb_4O_6 are amphoteric while Bi_2O_3 is basic.)
- $N_2O_5 > P_4O_{10} > As_4O_{10} > Sb_4O_{10}$

The oxides of nitrogen and phosphorus are discussed later.

3. Reactivity towards halogens (formation of halides)

Group 15 elements form two series of halides of the type EX_3 *(trihalides)* and EX_5 *(pentahalides)*. The trihalides are formed by all the elements while pentahalides are formed by all the elements except nitrogen. **Nitrogen cannot form pentahalides due to the absence of vacant *d*-orbitals in its outermost shell.** Similarly, the last element, Bi has little tendency to form pentahalides because +5 oxidation state of Bi is less stable than +3 oxidation state due to inert pair effect.

(*a*) Trihalides

All the elements of group 15 form trihalides of the general formula EX_3. All these trihalides are known (X = F, Cl, Br or I and E = N, P, As, Sb, Bi).

Structure. The valence shell electronic configuration of these elements is $ns^2\ np_x^1\ np_y^1\ np_z^1$ and all these elements undergo sp^3 hybridisation. The three of the four sp^3 hybrid orbitals overlap with *p* orbital of halogen atom to form three σ bonds with halogen atoms. The fourth sp^3 hybrid orbital contains the lone pair of electrons. Therefore, the geometry of trihalides may be regarded as **pyramidal**.

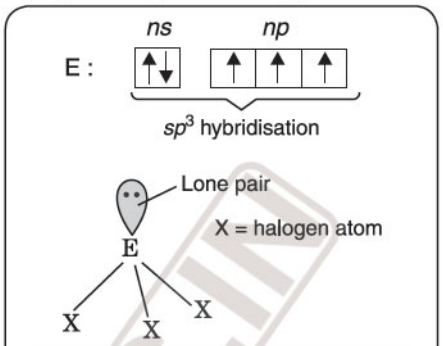

Fig. 5. Pyramidal shape of a trihalide of group 15.

The bond angles of the trihalides of an element increase as the electronegativity of the halogen decreases, *i.e.*,

PF_3	PCl_3	PBr_3	PI_3
96.3°	100.4°	101°	102°

Properties of trihalides (*i*) The trihalides of group 15 elements are predominantly covalent with the ionic character increasing down the group. For example, BiF_3 is ionic while other halides of Bi, *i.e.*, $BiCl_3$, $BiBr_3$, etc. and SbF_5 are partly covalent and partly ionic.

(*ii*) Out of all the trihalides, the trihalides of nitrogen are the least stable. Though **NF_3 is stable, NCl_3 is explosive**. NBr_3 and NI_3 are known only as their unstable ammoniates *i.e.*, $NBr_3.NH_3$ and $NI_3.NH_3$. Pure NBr_3 also explodes even at 173K. The nitrogen triiodide ammoniate is stable only in the moist state. In the dry state, it explodes with noise when struck liberating vapours of iodine.

$$8NI_3.NH_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$$

NCl_3, NBr_3 and NI_3 are unstable because N—X bond is weak due to large difference in the size of N and X atoms. However, NF_3 is stable because of small difference in size of N (75 pm) and F (72 pm) resulting strong N—F bond. As a result NF_3 is an exothermic compound. Because of stability of NF_3 it behaves quite differently from others. It is unreactive and does not hydrolyse with water, dilute acids or alkalies. However, it does react only when sparked with water vapour.

PF_3 is rather less reactive towards water and is more easily handled than the other halides.

(*iii*) The trihalides are easily hydrolysed by water. However, the products are different in hydrolysis of different chlorides.

$$NCl_3 + 3H_2O \longrightarrow NH_3 + \underset{\text{Hypochlorous acid}}{3HClO}$$

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$$PCl_3 + 3H_2O \longrightarrow \underset{\text{Phosphorous acid}}{H_3PO_3} + 3HCl$$

$$2AsCl_3 + 3H_2O \longrightarrow As_2O_3 + 6HCl$$

Antimony and bismuth trichlorides are only partially hydrolysed to form oxychlorides.

$$SbCl_3 + H_2O \rightleftharpoons \underset{\text{Antimony oxychloride}}{SbOCl\ (or\ SbO^+Cl^-)} + 2HCl$$

$$BiCl_3 + H_2O \rightleftharpoons \underset{\text{Bismuth oxychloride}}{BiOCl\ (or\ BiO^+Cl^-)} + 2HCl$$

It may be noted that in accordance with Le Chatelier principle, the excess of HCl suppresses the hydrolysis by shifting the equilibrium to the left.

(*iv*) The trihalides of P, As and Sb (especially fluorides and chlorides) act as Lewis acids and combine with Lewis bases :

$$PF_3 + F_2 \longrightarrow PF_5$$
$$SbF_3 + 2F^- \longrightarrow [SbF_5]^{2-}$$
$$SbCl_3 + 2Cl^- \longrightarrow [SbCl_5]^{2-}$$

The Lewis acid strength however, **decreases** in the order :

$$PCl_3 > AsCl_3 > SbCl_3 ; \quad PF_3 > PCl_3 > PBr_3 > PI_3$$

REMEMBER

In contrast to trihalides of P, As and Sb, the trihalides of nitrogen behave as **Lewis bases**. This is due to the absence of *d*-orbitals in N and the presence of lone pair of electrons. NF_3 has a little tendency to donate a pair of electrons and hence behaves as very weak Lewis base because of high electronegativity of fluorine. Fluorine is highly electronegative and has strong tendency to withdraw electrons from N. As a result, N-atom acquires partial positive charge and hence the tendency to donate electron pair of electrons decreases. Therefore, the Lewis base strength of trihalides of nitrogen increases as the electronegativity of halogen decreases, *i.e.*,

$$NF_3 < NCl_3 < NBr_3 < NI_3.$$

▶ The tendency of trihalides to act as Lewis base decreases from N to Bi for a given halide.

(*b*) Pentahalides

P, As and Sb form pentahalides of the general formula EX_5; EF_5 (E = P, As, Sb and Bi), ECl_5 (E = P, As and Sb) and PBr_5 and PI_5. As already studied, nitrogen does not form pentahalides because of the absence of *d*-orbitals in its valence shell.

The pentahalides of group 15 elements are thermally less stable than trihalides. This is due to the following reasons :

(*i*) As we go down the group, the stability of +5 oxidation state decreases while that of +3 oxidation state increases due to *inert pair effect*. Therefore, the ***pentahalides of Bi are not known except for BiF_5.***

(*ii*) As the size of halogen atom increases from F to I, the strength of E—X bond decreases and the steric hindrance increases. As a result, pentabromides and pentaiodides are unstable.

Therefore, the pentahalides of group 15 elements are less in number than trihalides. For example, pentafluorides of P, As, Sb and Bi are known, pentachlorides of only P, As, and Sb are known while bromides and iodides of only P are known.

Preparation. The pentahalides are prepared as :

$$3PCl_3 + 5AsF_3 \longrightarrow 3PF_5 + 5AsCl_3$$
$$PCl_3 + Cl_2\ (\text{in } CCl_4) \longrightarrow PCl_5$$
$$2As_2O_3 + 10F_2 \longrightarrow 4AsF_5 + 3O_2$$
$$2Sb_2O_3 + 10F_2 \longrightarrow 4SbF_5 + 3O_2$$
$$2Bi + 5F_2 \longrightarrow 4BiF_2$$

Structure. The pentahalides of group 15 elements have **trigonal bipyramidal** geometry in which the central atom is sp^3d hybridised. The three halogen atoms occupy equatorial positions while the other two occupy axial positions. This is not a regular structure because all the bond angles are not same. The axial bonds are at 90° while equatorial bonds are at 120° each. The axial positions experience greater repulsion than equatorial positions by bond pair of electrons. As a result, axial bonds are usually larger than the equatorial bonds. The structure of PF_5 is shown in Fig. 6 in which P—F axial bond lengths are 158 pm while P—F equatorial bond lengths are 153 pm.

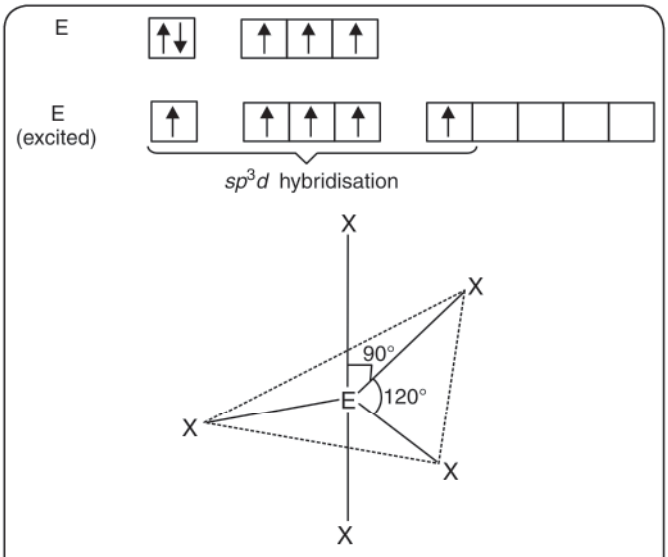

Fig. 6. Trigonal bipyramidal shape of EX_5 molecule.

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Properties (*i*) Pentahalides are thermally less stable than their corresponding trihalides. PF_5 is molecular in both the gaseous and solid states. PCl_5 exists as molecules in the gas phase but exists as $[PCl_4]^+$ $[PCl_6]^-$ in the crystalline state. PBr_5 and PI_5 also exist in the ionic form as $[PBr_4]^+$ $[PBr_6]^-$ and $[PI_4]^+I^-$ respectively in the solid state.

(*ii*) All the pentahalides behave as Lewis acids because of the presence of vacant *d*-orbitals. The central atom (except N) can accept a pair of electrons thereby expanding its coordination number to 6.

$$EX_5 + X^- \longrightarrow [EX_6]^-$$

During this the hybridisation of the central atom changes from sp^3d to sp^3d^2.

4. Reactivity towards metals

All the elements of group 15 combine with metals to form their binary compounds in which the elements show –3 oxidation state. For example, nitrogen forms **nitrides** (Mg_3N_2 : magnesium nitride, Ca_3P_2 : calcium nitride) arsenic forms **arsenides** (Na_3As : sodium arsenide), antimony forms **antimonides** (Zn_2Sb_3 : zinc antimonide) and bismuth forms **bismuthides** (Mg_3Bi_2 : magnesium bismuthide).

ANOMALOUS BEHAVIOUR OF NITROGEN

Nitrogen, the first member of group 15, differs from its rest of family members. This may be due to :

(*i*) its small size.

(*ii*) its high ionisation enthalpy and electronegativity.

(*iii*) absence of *d*-orbitals in its valence shell.

Some of the characteristics in which nitrogen differs from other family members are given below :

(*i*) Nitrogen is a gas at room temperature while the rest of the members of the family are solids.

(*ii*) Nitrogen does not exhibit pentavalency in its compounds while other members show pentavalency.

(*iii*) Nitrogen has a tendency to form $p\pi$-$p\pi$ bonds and exists as N_2 molecule while other elements do not have such tendency. Instead, they prefer to form single bonds as P–P, As–As etc.

(*iv*) Due to the absence of *d*-orbitals in the valence shell, nitrogen cannot form $d\pi$-$p\pi$ bonds and therefore, compounds of the type $R_3N=O$ and $R_3N=CH_2$ are not known. However, P and arsenic form compounds such as $R_3P=O$, $R_3P=CH_2$ containing $d\pi$-$p\pi$ bonds.

(*v*) The hydride of nitrogen (NH_3) is more basic than the hydrides of the other members of the family.

(*vi*) Nitrogen does not form any complex whereas the other members form complexes.

(*vii*) Nitrogen can form hydrogen bonds in its compounds and rest of the members do not form hydrogen bonds due to small electronegativities.

(*viii*) Nitrogen forms a variety of the oxides while the other members form trioxides and pentoxides only.

(*ix*) Except NF_3, the trihalides of nitrogen (NCl_3, NBr_3 and NI_3) are explosive. The trihalides of other elements are, however, stable.

SOLVED EXAMPLES

Example 1.

Nitrogen exists as diatomic molecule and phosphorus exists as tetraatomic molecule, P_4. Explain.

N.C.E.R.T. *(Pb. S.B. 2015, H.P.S.B. 2014, 2016)*

Solution : The size of nitrogen atom is quite small. As a result, two nitrogen atoms can be linked to each other by three covalent bonds in order to complete the octets of both the nitrogen atoms as : N ≡ N :. However, phosphorus being large in size has less tendency to form three bonds. Therefore, P atom completes its octet by sharing its valence electrons with three other P atoms. As a result, it exists as P_4 molecule.

Example 2.

Though nitrogen exhibits + 5 oxidation state, it does not form pentahalides. Give reason.

N.C.E.R.T. *(A.I.S.B. 2013, D.S.B. 2015, 2017)*

Solution : Nitrogen belongs to second period ($n = 2$) and has only *s* and *p*-orbitals. It does not have *d*-orbitals in its valence shell and therefore, it cannot extend its octet. That is why nitrogen does not form pentahalides.

Example 3.

Why is N_2 less reactive at room temperature ?

(Pb.S.B. 2013, A.I.S.B. 2015, H.P.S.B. 2015, 2016, Meghalaya S.B. 2017)

Solution : In molecular nitrogen, there is a triple bond between two nitrogen atoms (N ≡ N) and it is non-polar in character. Due to the presence of a triple bond, it has very high bond dissociation energy (941.4 kJ mol^{-1}) and therefore, it does not react with other elements under normal conditions and is very unreactive. However, it may react at higher temperatures.

Example 4.

Phosphine has lower boiling point than ammonia. Give reason.

N.C.E.R.T. *(A.I.S.B. 2008, D.S.B.2013, Mizoram S.B.2013, Uttarakhand S.B. 2014, H.P.S.B. 2015, Hr. S.B. 2017)*

Solution : Ammonia exists as associated molecule due to its tendency to form hydrogen bonding. Therefore, it has high boiling point. Unlike NH_3,

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phosphine (PH_3) molecules are not associated through hydrogen bonding in liquid state. This is because of low electronegativity of P than N. As a result, the boiling point of PH_3 is lower than that of NH_3.

❑ **Example 5.**

Unlike phosphorus, nitrogen shows little tendency for catenation.

Solution : Nitrogen has little tendency for catenation because N—N single bond is weak. This is because nitrogen has small size and the lone pairs on two nitrogen atoms repel each other. On the other hand, phosphorus is comparatively large in size so that lone pairs on P atoms donot repel to the same extent. As a result P—P bond is stronger than N—N bond. Therefore, P has a tendency for catenation because of high bond enthalpy of P—P bond.

❑ **Example 6.**

Out of Bi(V) and Sb(V) which may be a stronger oxidising agent and why ? *(D.S.B. 2008)*

Solution : On moving down the group, the stability of +5 oxidation state decreases while the stability of +3 oxidation state increases due to inert pair effect. Therefore, +5 oxidation state of Bi is less stable than +5 oxidation state of Sb. Thus, Bi(V) is a stronger oxidising agent than Sb(V).

Practice Problems

1. Which of the two : PH_3 or NH_3 is more basic ?
2. Which hydride of group 15 elements has lowest boiling point ?
3. Name three allotropes of phosphorus. Which of these is most reactive ?
4. Which of the two : NH_3 or PH_3 is soluble in water ?
5. Arrange BiH_3, PH_3 and NH_3, in the increasing order of their reducing character.

Answers to Practice Problems

1. NH_3
2. PH_3
3. Red, black, white or yellow. White P is most reactive.
4. NH_3
5. $NH_3 < PH_3 < BiH_3$

CHEMISTRY OF NITROGEN AND ITS COMPOUNDS

DINITROGEN

Nitrogen was discovered *by Daniel Rutherford* in 1772. It is the first member of group 15 of the periodic table. It has the electronic configuration $1s^2\ 2s^2\ 2p^3$ and therefore, has five electrons in its valence shell. In the molecular form, it exists as a diatomic molecule (N_2) having triple bond between nitrogen atoms ($N \equiv N$). Therefore, it is also referred to as *dinitrogen*. It is a typical non-metal with high electronegativity next only to fluorine and oxygen.

Preparation of Dinitrogen

In the **laboratory**, dinitrogen is prepared by heating an aqueous solution containing an equivalent amount of ammonium chloride and sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \xrightarrow{\text{Heat}} N_2(g) + 2H_2O(l) + NaCl(aq)$$

During the preparation, small amounts of NO and HNO_3 are also formed in the reaction. These impurities can be removed by bubbling the gas through aqueous sulphuric acid containing a small amount of potassium dichromate.

It can also be prepared by

(*i*) *Thermal decomposition of ammonium dichromate.*

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} Cr_2O_3 + N_2 + 4H_2O$$

(*ii*) *By the action of ammonia with cupric oxide or bleaching powder.*

$$2NH_3 + 3CuO \xrightarrow{\text{Heat}} 3Cu + N_2 + 3H_2O$$

$$2NH_3 + 3CaOCl_2 \xrightarrow{\text{Heat}} 3CaCl_2 + N_2 + 3H_2O$$

Bleaching powder

(*iii*) **Very pure nitrogen** can be obtained by the thermal decomposition of sodium or barium azide

$$2NaN_3 \xrightarrow{573\ K} 2Na + 3N_2$$

Sodium azide

$$Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba + 3N_2$$

Barium azide

REMEMBER

Thermal decomposition of sodium azide is used to inflate the air bags used for safety devices in some cars.

Commercial Isolation of Dinitrogen from Air

Commercially dinitrogen is prepared by the liquefaction and fractional distillation of air. Air contains dinitrogen (*b.p.* 77.2 K) and dioxygen (*b.p.* 90 K). When the liquid air is allowed to boil, dinitrogen with lesser boiling point gets distilled first leaving behind dioxygen. The dinitrogen obtained from air contains traces of oxygen and some other gases as impurities.

Properties of Dinitrogen

Physical Properties

(*i*) Dinitrogen is a *colourless, odourless* and *tasteless* gas.

(*ii*) It has two stable isotopes ^{14}N and ^{15}N.

(*iii*) It is a non-toxic gas.

(*iv*) It is slightly lighter than air and its vapour density is 14.

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(*v*) It has very low solubility in water (about 23.2 cm^3 per litre of water at 1 atmosphere pressure and 273 K).

(*vi*) Its melting and boiling points are low; 63.2 K and 77.2 K respectively.

Chemical Properties

Dinitrogen is chemically *unreactive* at room temperature. It is neither combustible nor it supports combustion. The N—N bond in nitrogen molecule is a triple bond (N ≡ N) with a bond distance of 109.8 pm and bond dissociation enthalpy of 941.4 kJ mol^{-1}. *The low reactivity of nitrogen is due to very small size of the molecule and high bond dissociation enthalpy of the molecule.* However, reactivity increases rapidly with the rise in temperature. At higher temperature dinitrogen combines with some metals to form predominantly ionic nitrides and with non-metals to form covalent nitrides.

1. Action with litmus. Dinitrogen is neutral towards litmus because it has no action on blue or red litmus.

2. Action with metals. It combines with a number of active metals on strong heating to form their respective nitrides. For example,

$$6Li + N_2 \xrightarrow{Heat} \underset{\text{Lithium nitride}}{2Li_3N}$$

$$3Mg + N_2 \xrightarrow{Heat} \underset{\text{Magnesium nitride}}{Mg_3N_2}$$

$$3Ca + N_2 \xrightarrow{Heat} \underset{\text{Calcium nitride}}{Ca_3N_2}$$

$$2Al + N_2 \xrightarrow{Heat} \underset{\text{Aluminium nitride}}{2AlN}$$

3. Combination with non-metals. Dinitrogen combines with non-metals like dioxygen and dihydrogen.

(*i*) Combination with dihydrogen. Dinitrogen reacts with dihydrogen at about 700 K under a pressure of 200 atm in the presence of iron as catalyst (Haber process). A small amount of molybdenum is also used as a promotor.

$$N_2 + 3H_2 \xrightarrow[700\ K,\ 200\ atm\ pressure]{Fe,\ Mo} \underset{\text{Ammonia}}{2NH_3} \qquad \Delta_f H^{\ominus} = -46.1\ kJ\ mol^{-1}$$

(*ii*) Combination with dioxygen. Dinitrogen combines with dioxygen during lightning or at high temperature of about 2000 K and form nitric oxide.

$$N_2 + O_2 \xrightarrow{>2000\,K} \underset{\text{Nitric oxide}}{2NO} \qquad \Delta_r H^{\ominus} = 135\ kJ\ mol^{-1}$$

Nitric oxide is a colourless gas but is very unstable. It immediately reacts with more of oxygen to form nitrogen dioxide.

$$2NO + O_2 \longrightarrow 2NO_2$$

4. Combination with compounds. Dinitrogen also combines with certain compounds on strong heating. For example,

With calcium carbide

$$\underset{\text{Calcium carbide}}{CaC_2} + N_2 \xrightarrow{1300\,K} \underset{\text{Calcium cyanamide}}{CaCN_2} + \underset{\text{Carbon}}{C}$$

With alumina in the presence of carbon

$$\underset{\text{Aluminium oxide}}{Al_2O_3} + N_2 + 3C \xrightarrow{1273\,K} \underset{\text{Aluminium nitride}}{2AlN} + 3CO$$

Both these compounds are hydrolysed on boiling with water to give ammonia.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

Therefore, *calcium cyanamide is used as a fertilizer under the name* **nitrolim** ($CaCN_2 + C$).

R U Curious ...

❑ How do airbags installed in the dash board of your car work?

▶ An airbag is a vehicle safety device. Its purpose is to provide protection to the occupants when they strike interior objects such as steering wheel, window, dashboard, etc. during accidents. The airbag is made of a thin nylon fabric and contains sodium azide (NaN_3). When accident occurs, the impact sensors provided in the car detect the collision. These sensors send an electrical signal which overheats and ignites sodium azide (NaN_3) placed in the airbag. Sodium azide is a fast burning fuel and within about 20–30 milliseconds of impact, it decomposes to produce N_2 gas.

$$2NaN_3 \longrightarrow 2Na + 3N_2$$

The N_2 gas produced passes through filters and fills the nylon airbag and inflates it. The airbag then hits the car's occupant and protects him from injury. After hitting, the airbag deflates immediately and the gas escapes through tiny holes in the fabric (or as it is sometimes called the cushion) and cools. Deployment is accompanied by release of dust like particles usually talcum powder or corn starch which are used to lubricate the airbag during deployment. The powder protects the bag from sticking to itself, while it is folded inside the car. The N_2 gas released is absolutely harmless. The only precaution is to open the door and windows for good ventillation to avoid the affect of dust particles. It may be noted that some airbag manufacturers mix sodium azide with other chemicals that will react with sodium and form less toxic compounds.

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Uses of Dinitrogen

(*i*) Dinitrogen is used in the manufacture of compounds like ammonia, nitric acid, calcium cyanamide, etc.

(*ii*) It is used in providing inert atmosphere in iron and steel industries.

(*iii*) Liquid nitrogen is used as refrigerant to preserve biological specimens, in freezing food stuffs and also in cryosurgery.

(*iv*) It is used in gas-filled thermometers used for measuring high temperatures.

(*v*) Dinitrogen is used in filling electric bulbs to reduce the rate of volatilisation of the tungsten filament.

Fixation of Nitrogen

The process of conversion of atmospheric dinitrogen into useful compounds is called **nitrogen fixation**. Fixation of nitrogen is brought about in the following ways :

- During lightning and thunder storms the energy in lightning allows nitrogen and oxygen to combine to form oxides of nitrogen which are washed into the soil and are taken up by the plants as nitrates. As animals live on plants, they are transferred to the animal bodies where a series of metabolic changes take place.
- The atmospheric nitrogen can be converted into useful compounds (which can be used by plants) by the action of certain *bacteria* and *algae*. All types of bacteria are not able to fix nitrogen. The *symbiotic bacteria* present in the root nodules of leguminous plants (*e.g.*, peas, beans, grams, etc.) catch up the nitrogen from the atmosphere and supplies to the plant, which in turn give food to the bacteria. The non-leguminous plants like *Alnus, Ginkgo* also fix atmospheric nitrogen. Certain blue-green algae found in paddy fields is also able to fix nitrogen. These biochemical processes involve an enzyme called **nitrogenase** in which the active sites contain molybdenum and iron atoms.
- Dinitrogen can be made to take part in different chemical reactions under suitable conditions to prepare useful compounds. This is called **artificial fixation**.

The common examples of industrial fixation of nitrogen is the manufacture of ammonia by Haber's process. In this process, a large amount of atmospheric nitrogen is fixed in the form of NH_3.

AMMONIA

Ammonia is the most important compound of nitrogen. It is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter *e.g.*, urea.

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$$
Urea
$$\rightleftharpoons 2NH_3 + CO_2 + H_2O$$

Laboratory Preparation

Ammonia is prepared in the laboratory by heating ammonium salt; NH_4Cl or $(NH_4)_2SO_4$ with a strong alkali like NaOH.

$$NH_4Cl + NaOH \longrightarrow NH_3 + H_2O + NaCl$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

It can also be prepared by heating ammonium chloride with slaked lime.

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{Heat} CaCl_2 + 2NH_3 + 2H_2O$$
Slaked lime

It can also be prepared by the hydrolysis of magnesium nitride.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

Ammonia can be dried by passing over quicklime (CaO). *However, it cannot be dried with dehydrating agents such as conc. H_2SO_4, P_2O_5 and anhydrous $CaCl_2$ because ammonia reacts with these compounds.*

Manufacture of ammonia

Ammonia can be manufactured by **Haber's process** which involves the reaction :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);$$
$$\Delta H^\circ = -92.2 \text{ kJ mol}^{-1}$$
or $$\Delta_f H^\circ(NH_3) = -46.1 \text{ kJ mol}^{-1}$$

This is a reversible exothermic reaction. The favourable conditions for high yield of ammonia can be understood by applying *Le Chatelier's principle.*

***(i)* Low temperature.** Since the forward reaction is exothermic, therefore, low temperature will favour the formation of ammonia. However, *an optimum temperature of about 700 K is necessary.*

***(ii)* High pressure.** High pressure of the order of 200 atmospheres or 200×10^5 Pa is required to favour the forward reaction.

***(iii)* Presence of catalyst.** The use of catalyst such as iron oxide containing a small amounts of molybdenum or potassium oxide (K_2O) and aluminium oxide (Al_2O_3) as promoter, increases the rate of attainment of equilibrium of ammonia.

Details of the process

The plant required for the manufacture of ammonia is shown in Fig. 7.

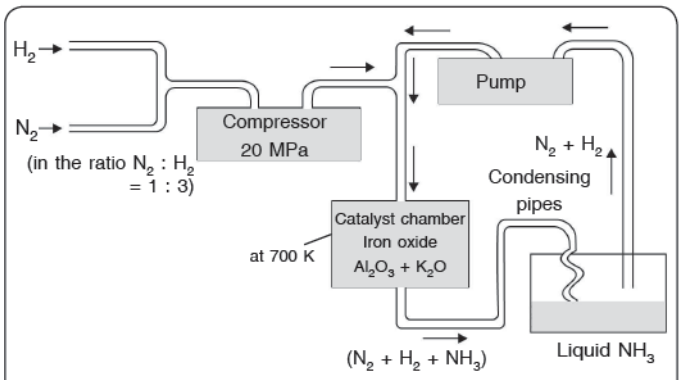

Fig. 7. Flow chart for Haber's process for the manufacture of ammonia.

In this method, a mixture of N_2 and H_2 in the molar ratio of 1 : 3 is compressed to about 200 atmosphere pressure. The compressed gases are then cooled and passed through soda lime tower to free them from moisture and carbon dioxide. Then these are fed into catalyst chamber packed with iron oxide with small amount of K_2O and $A1_2O_3$ or molybdenum. The chamber is heated electrically to a temperature of 700 K when the two gases combine to form ammonia. The reaction being exothermic, the heat evolved maintains the desired temperature and further electrical heating is not required.

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The gases which escape from the chamber contain about 15–20% ammonia and the remaining are unreacted N_2 and H_2. These are passed through condensing pipes where ammonia gets liquefied and is collected in the receiver. The unreacted gases are pumped back to the compression pump where they are mixed with fresh gaseous mixture.

Structure of ammonia. Ammonia is expected to have a tetrahedral geometry because the central nitrogen atom involves sp^3 hybridisation as already discussed. It has one position occupied by a lone pair. The lone pair distorts its geometry and the molecule has **pyramidal geometry** with nitrogen atom at the apex. The N—H bond length is 101.7 pm and HNH bond angle is 107.8°.

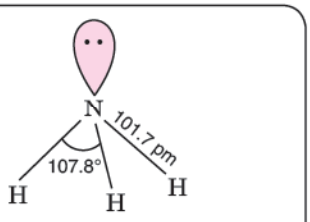

Fig. 8. Structure of ammonia.

Properties of Ammonia

Physical properties (*i*) Ammonia is a *colourless gas* with a *characteristic* pungent smell called ammoniacal smell.

(*ii*) It is lighter than air (density = 0.68 g/cm^3)

(*iii*) It is highly soluble in water; one volume of water can dissolve about 1000 volumes of the gas at 273 K. The high solubility of ammonia in water is due to its tendency to form intermolecular hydrogen bonding.

(*iv*) Ammonia can be easily liquefied under pressure. Liquid ammonia has b.p. 239.7 K and f.p. 198.4 K. Like water, ammonia is also associated in the solid and liquid states through hydrogen bonds. This accounts for its higher melting and boiling points than expected on the basis of its molecular mass.

Chemical properties

1. Basic nature. Ammonia gas is highly soluble in water. Its aqueous solution turns red litmus blue indicating its weakly basic character. The basic character of ammonia is due to the formation of OH^- ions in aqueous solution.

$$NH_3\,(aq) + H_2O\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

Being basic ammonia forms salts with both weak and strong acids such as NH_4Cl, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, etc.

$$NH_3\,(aq) + HCl\,(aq) \longrightarrow NH_4Cl\,(s)$$
$$2NH_3(aq) + H_2SO_4 \longrightarrow (NH_4)_2SO_4(s)$$

2. As a Lewis base : tendency to form complexes. Ammonia acts as a ***Lewis base*** due to the presence of lone pair of electrons on the nitrogen atom. Therefore, it can form coordinate bond with electron deficient molecules (such as BF_3) or a number of transition metal cations forming *complex compounds*. For example,

$$BF_3 + NH_3 \longrightarrow BF_3 \leftarrow NH_3$$

$$Ag^+\,(aq) + 2NH_3\,(aq) \longrightarrow \underset{\text{Colourless}}{[Ag(NH_3)_2]^+\,(aq)}$$

$$Cu^{2+}\,(aq) + 4NH_3\,(aq) \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}\,(aq)}$$

$$Cd^{2+} + 4NH_3 \longrightarrow [Cd(NH_3)_4]^{2+}\,(aq)$$

Since ammonia forms complexes, the white precipitate of silver chloride dissolves in excess of ammonium hydroxide to form a soluble complex.

$$\underset{\text{White ppt.}}{AgCl} + 2NH_4OH \rightleftharpoons \underset{\substack{\text{Diamminesilver (I)}\\ \text{chloride (colourless)}}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

Similarly, copper sulphate dissolves in excess of ammonium hydroxide to form deep blue coloured complex.

$$CuSO_4 + 4NH_4OH \rightleftharpoons \underset{\substack{\text{Tetraamminecopper (II)}\\ \text{sulphate (Blue)}}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

The formation of such complex compounds finds applications in detection of metal ions (Ag^+, Cu^+, etc.)

3. Action with halogens. (*i*) Chlorine reacts with ammonia in two ways depending upon whether ammonia is in excess or chlorine is in excess.

Excess NH_3 :

$$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

Excess Cl_2 :

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

Bromine also reacts in a similar way.

Excess of ammonia :

$$8NH_3 + Br_2 \longrightarrow 2NH_4Br + 3N_2$$

Excess of bromine :

$$NH_3 + 3Br_2 \longrightarrow NBr_3 + 3HBr$$

(*ii*) Iodine reacts with liquid ammonia to form a dark brown complex.

$$2NH_3 + 3I_2 \longrightarrow \underset{\substack{\text{Nitrogen tri-iodide}\\ \text{ammoniate (brown complex)}}}{NH_3NI_3} + 3HI$$

The complex is very explosive when dry. It explodes violently when rubbed against a hard surface as follows :

$$8NH_3NI_3 \xrightarrow{\text{Heat}} 5N_2 + 9I_2 + 6NH_4I$$

4. Oxidation. Ammonia is oxidised to dinitrogen with oxidising agents like CuO, NaClO, $Ca(OCl)_2$ etc. For example, when ammonia is passed over heated copper oxide, it gets oxidised to dinitrogen.

$$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$$

Similarly, $4NH_3 + 3Ca(OCl)_2 \longrightarrow 2N_2 + 3CaCl_2 + 6H_2O$

When vapours of NH_3 and O_2 are passed over red hot platinum gauze at 1075 K, it is oxidised to niric oxide.

$$4NH_3 + 5O_2 \xrightarrow[1075\text{ K}]{\text{Pt}} \underset{\text{Nitric oxide}}{4NO} + 6H_2O$$

This reaction forms the basis of Ostwald's process for the manufacture of nitric acid.

5. Combustion. Ammonia is neither combustible nor supporter of combustion. However, it burns in the presence of oxygen to form dinitrogen and water.

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

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6. Formation of amides. When ammonia is passed over heated sodium or potassium at 575 K, it forms amides with the liberation of dihydrogen.

$$2Na + 2NH_3 \xrightarrow{575K} \underset{\text{Sodamide}}{2NaNH_2} + H_2$$

$$2K + 2NH_3 \xrightarrow{575K} \underset{\text{Potassium amide}}{2KNH_2} + H_2$$

7. Precipitation of heavy metal ions from the aqueous solution of their salts. Heavy metal ions such as Fe^{3+}, Cr^{3+}, Al^{3+}, etc. are precipitated from their aqueous salt solutions as hydroxides with ammonia.

$$FeCl_3(aq) + 3NH_4OH(aq) \longrightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3(s)} + 3NH_4Cl(aq)$$

$$AlCl_3(aq) + 3NH_4OH(aq) \longrightarrow \underset{\text{White ppt.}}{Al(OH)_3(s)} + 3NH_4Cl(aq)$$

$$CrCl_3(aq) + 3NH_4OH(aq) \longrightarrow \underset{\text{Green ppt.}}{Cr(OH)_3(s)} + 3NH_4Cl(aq)$$

$$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2(s)} + (NH_4)_2SO_4(aq)$$

Tests of ammonia

- Ammonia can be tested by its reaction with Nessler's reagent. It gives brown precipitate with Nessler's reagent (an alkaline solution of K_2HgI_4) due to the formation of iodide of Million's base.

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow \underset{\text{Iodide of Million's base (brown ppt).}}{H_2N - Hg - O - Hg - I} + 7KI + 2H_2O$$

(Nessler's reagent)

- With a drop of HCl, it produces dense white fumes of ammonium chloride.
- It turns moist red litmus paper blue and moist turmeric paper brown.
- It gives a yellow precipitate with chloro-platinic acid.

$$\underset{\text{Chloroplatinic acid}}{H_2PtCl_6} + 2NH_3 \longrightarrow \underset{\text{Ammonium chloroplatinate (yellow ppt.)}}{(NH_4)_2PtCl_6}$$

Uses of ammonia

(*i*) It is used in the manufacture of nitric acid and sodium carbonate.
(*ii*) Liquid ammonia is used as a refrigerant.
(*iii*) It is used in the manufacture of rayon.
(*iv*) It is commonly used for preparing various nitrogenous fertilizers such as ammonium nitrate, ammonium sulphate, ammonium phosphate and urea.
(*v*) It is an important reagent and is used as a solvent in the laboratory.

OXIDES OF NITROGEN

Nitrogen combines with oxygen under different conditions to form a number of binary oxides which differ with respect to the oxidation state of the nitrogen atom. They range from N_2O (oxidation state of N +1) through NO (+2), N_2O_3 (+3), N_2O_4 (+4) to N_2O_5 (5). The tendency to form $p\pi$—$p\pi$ multiple bonds dictates the structures of oxides. The important oxides are NO, N_2O_3, NO_2, N_2O_4 and N_2O_5.

The molecular formulae of various oxides of nitrogen are given in Table 5.

Table 5. Oxides of nitrogen.

Oxide	Oxidation state of N	Physical appearance acidic or neutral character	Properties
N_2O Dinitrogen monoxide Nitrous oxide or Nitrogen (I) oxide	+ 1	Colourless gas Neutral	Unreactive gas
NO Nitric oxide or Nitrogen (II) oxide	+ 2	Colourless Neutral	Paramagnetic, reactive and thermodynamically unstable
N_2O_3 Dinitrogen trioxide or Nitrogen (III) oxide	+ 3	Pale blue solid Acidic	Unstable in gaseous phase
N_2O_4 Dinitrogen tetroxide or Nitrogen (IV) oxide	+ 4	Colourless solid or liquid Acidic	Exists in equilibrium with NO_2 both in gaseous and liquid state
NO_2 Nitrogen dioxide or Nitrogen (IV) oxide	+ 4	Brown gas Acidic	Reactive and paramagnetic
N_2O_5 Dinitrogen pentoxide or Nitrogen (V) oxide	+ 5	Colourless solid or gas Acidic	Unstable as gas, in solid state exists as $[NO_2]^+ [NO_3]^-$

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1. Nitrous oxide (N_2O). It is prepared by heating ammonium nitrate.

$$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$$

It is a colourless unreactive gas having faint pleasant smell. It is also known as *laughing gas* because it causes *hysterical laughter* when inhaled in minor quantities. It is a neutral oxide and reacts with sodamide to form sodium azide.

$$N_2O + 2NaNH_2 \longrightarrow \underset{\text{Sodamide}}{NaN_3} + \underset{\text{Sod. azide}}{NH_3} + NaOH$$

In small amounts, it acts as an anaesthetic for minor operations.

It decomposes into nitrogen and oxygen at 873 K.

$$2N_2O \longrightarrow 2N_2 + O_2$$

Therefore, it supports the combustion acting as a source of oxygen.

Nitrous oxide (N_2O) is known as **laughing gas** because it causes hysterical laughter when inhaled in minor quantities.

2. Nitric oxide (NO). It is prepared by the catalytic oxidation of ammonia at 1100 K in the presence of platinum.

$$4NH_3 + 5O_2 \xrightarrow[\text{Pt}]{1100\ K} 4NO + 6H_2O$$

It can also prepared by the reaction of nitric acid on copper as :

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

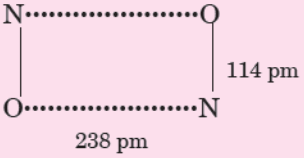
It can also be prepared by the reduction of sodium nitrite with ferrous sulphate in the presence of sulphuric acid.

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$

It is a neutral oxide.

The largest use of N_2O is as **propellant** for whipped ice-cream. Because it has no taste, and is non-toxic and therefore, it meets the strict food and health regulations.

It is a colourless gas. It has odd number of electrons (11 valence electrons) and therefore, it is paramagnetic in the gaseous state. However, in the liquid and solid states, it forms a loose dimer in such a way that the magnetic effects of two unpaired electrons are cancelled out. The molecule is diamagnetic.



Nitric oxide due to the presence of an odd electron, is very reactive. It readily reacts with oxygen to give brown fumes of nitrogen dioxide and with halogens to give nitrosyl halides.

$$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2\ (g)$$

$$2NO + Cl_2 \longrightarrow \underset{\text{Nitrosyl chloride}}{2NOCl}$$

Nitric oxide readily forms complexes with transition metals. For example, Fe^{2+} combines with NO to form the complex $[Fe(H_2O)_5NO]^{2+}$ which is responsible for the colour in *brown ring test for nitrates*.

It is thermodynamically unstable and decomposes into elements at high temperatures (1373 K – 1473 K)

$$2NO\ (g) \xrightarrow{1373-1473\ K} N_2\ (g) + O_2\ (g)$$

3. Dinitrogen trioxide (N_2O_3). It is prepared by cooling equimolar quantities of nitric oxide and nitrogen dioxide to below 253 K.

$$NO(g) + NO_2(g) \underset{}{\overset{253\ K}{\rightleftharpoons}} N_2O_3$$

It can also be prepared by reacting nitric oxide and dinitrogen tetraoxide at 250 K.

$$2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$$

It is a blue solid and is acidic in nature. It is anhydride of nitrous acid (HNO_2).

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

It exists in the pure form only in the solid state at very low temperatures. Above its melting point (273 K) it dissociates to NO and NO_2.

$$\underset{\text{Blue}}{N_2O_3} \xrightarrow{\text{Above 173 K}} \underset{\text{Colourless}}{NO} + \underset{\text{Brown}}{NO_2}$$

4. Nitrogen dioxide (NO_2). It is prepared by heating dried lead nitrate in a steel reaction vessel.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

It is also an odd electron molecule and in the gas phase, it exists in equilibrium with N_2O_4 as :

$$\underset{\text{Colourless}}{N_2O_4} \rightleftharpoons \underset{\text{Brown}}{2NO_2}$$

Above 415 K, it contains mainly NO_2 and at 250 K, it consists of mainly N_2O_4.

$$2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$$

5. Dinitrogen pentoxide (N_2O_5). It is prepared by dehydrating the concentrated nitric acid with phosphorus pentoxide.

$$4HNO_3 + \underset{\text{Phosphorus pentoxide}}{P_4O_{10}} \longrightarrow 2N_2O_5 + \underset{\text{Metaphosphoric acid}}{4HPO_3}$$

N_2O_5 exists as colourless solid below 273K. As the temperature rises, the colour changes to yellow due to the partial decomposition of colourless N_2O_5 to brown NO_2.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

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At 303 K, the crystals melt giving a yellow liquid which decomposes at 313 K to give NO_2.

N_2O_5 acts as a strong oxidising agent and oxidises iodine to I_2O_5.

The oxides of nitrogen N_2O_3, NO_2, N_2O_5 are acidic and react with water to give oxoacids of nitrogen. For example, N_2O_3 gives nitrous acid (HNO_2) while N_2O_5 give nitric acid (HNO_3).

$$N_2O_3 + H_2O \longrightarrow \underset{\text{Nitrous acid}}{2HNO_2}$$

$$N_2O_5 + H_2O \longrightarrow \underset{\text{Nitric acid}}{2HNO_3}$$

Therefore, N_2O_3 is regarded as anhydride of nitrous acid and N_2O_5 is regarded as anhydride of nitric acid. Nitrogen dioxide (NO_2) reacts with water to give both nitrous acid and nitric acid.

$$2NO_2 + H_2O \longrightarrow \underset{\text{Nitrous acid}}{HNO_2} + \underset{\text{Nitric acid}}{HNO_3}$$

Therefore, NO_2 is a mixed anhydride of nitric acid and nitrous acid.

Out of various oxides, NO and NO_2 are used in the manufacture of nitric acid and nitrate fertilizers. Liquid N_2O_4 is also used as an oxidiser for the rocket fuels in missiles and space vehicles. However, NO causes a pollution problem in atmosphere due to its poisonous nature. Its vapours are emitted in the atmosphere during the burning of oil and coal.

Oxides of nitrogen are emitted into the atmosphere during burning of coal and oil in power stations and automobile engines. These are also present in the automobile exhausts. These cause air pollution in major cities and near power stations. These oxides of nitrogen also cause **acid rain** and **photochemical smog** (discussed in class XI in environmental chemistry).

R U Curious ...

- **You will be surprised to note that though nitric oxide (NO) is very reactive and harmful, yet it occurs in biological systems in traces.**
- It acts as a **neuro-transmitter** and plays a significant role in controlling blood pressure by relaxing blood vessels. It also protects from bacterial infections.

The general methods of preparation of nitrogen oxides are summed up below:

SUM UP

Oxide of nitrogen	Common method of preparation
N_2O	*(i)* $NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$
	(ii) $HNO_2 + NH_2OH\ (aq) \longrightarrow N_2O + 2H_2O$
NO	*(i)* $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
	(ii) $4NH_3 + 5O_2 \xrightarrow[\text{Pt catalyst}]{1100\ K} 4NO + 6H_2O$
	(iii) $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + +2NO + 2H_2O$
N_2O_3	$NO + NO_2 \longrightarrow N_2O_3$
	$2NO + N_2O_4 \xrightarrow{< 250\ K} 2N_2O_3$
N_2O_4	$2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$
NO_2	*(i)* $2Pb(NO_3)_2 \xrightarrow{673\ K} 2PbO + 4NO_2 + O_2$
	(ii) $Cu + 4HNO_3(\text{conc.}) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
N_2O_5	$P_4O_{10} + 4HNO_3 \longrightarrow 2N_2O_5 + 4HPO_3$

The molecular and Lewis dot stuructures of oxides of nitrogen are given ahead.

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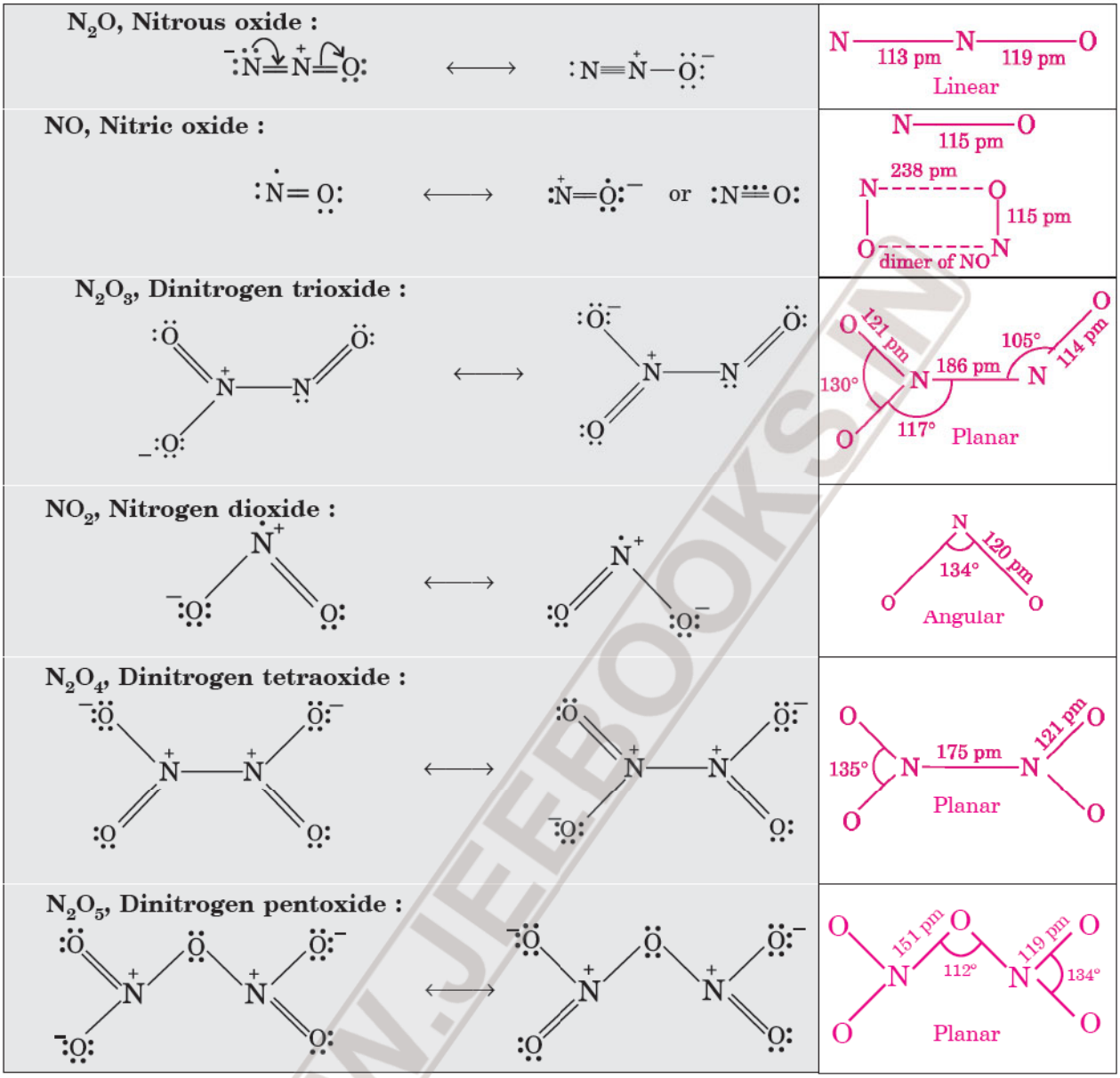
N_2O, Nitrous oxide :



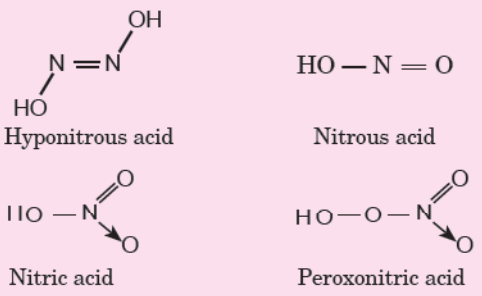
NITRIC ACID (HNO_3)

Nitrogen forms numerous oxoacids though several are unstable in the free state and are known only in aqueous solution or as their salts. The common oxoacids of nitrogen are given below :

Table 6. Oxoacids of nitrogen.

Name	Formula	Oxidation State of N	Nature
Hyponitrous acid	$H_2N_2O_2$	+2	weak acid known as its salts
Nitroxylic acid	$H_4N_2O_4$	+2	highly explosive difficult to get in pure state
Nitrous acid	HNO_2	+3	weak acid and unstable
Nitric acid	HNO_3	+5	weak acid and stable
Peroxonitric acid	HNO_4	+5	unstable and explosive

Oxoacids of nitrogen



Out of the oxoacids of nitrogen, **nitric acid is the most important**. It is very strong oxidising agent and is quite useful. Nitrogen shown an oxidation state of +5 in nitric acid.

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Laboratory preparation of nitric acid. In the laboratory, nitric acid can be prepared by heating sodium or potassium nitrate with concentrated sulphuric acid to about 423–475 K

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

Anhydrous nitric acid can be obtained by distillation of concentrated aqueous nitric acid with P_4O_{10}.

Manufacture of Nitric Acid

Nitric acid is commonly manufactured by **Ostwald process** in which it is prepared by the catalytic oxidation of ammonia by atmospheric oxygen. The reaction is carried out at about 500 K and 9×10^5 Pa (9 bar) pressure in the presence of Pt or Rh gauge as catalyst.

$$4NH_3(g) + 5O_2(g) \xrightarrow[500K,\ 9\ bar]{Pt/Rh\ gauge} 4NO(g) + 6H_2O(g)$$

(from air) $\Delta H = -90.2$ kJ

Nitric oxide thus formed combines with oxygen to form nitrogen dioxide.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Nitrogen dioxide so formed, dissolves in water to give nitric acid.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

The NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto about 68% by mass.

Dilute nitric acid is further concentrated by dehydration with concentrated sulphuric acid to get about 98% acid.

Properties of Nitric acid

Physical Properties

(*i*) Pure nitric acid is a *colourless liquid*.

(*ii*) It has boiling point 355.6 K and freezing point 231.4 K.

(*iii*) Laboratory grade nitric acid contains about 68% of HNO_3 by mass and has a specific gravity of 1.504.

(*iv*) The impure acid is generally yellow due to the presence of nitrogen dioxide as impurity. Nitric acid containing dissolved nitrogen dioxide is known as *fuming nitric acid*.

(*v*) It has a corrosive action on skin and produces painful *blisters*.

Chemical Properties

1. Acidic character. It is one of the strongest acids because it is highly ionised in aqueous solution giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+ + NO_3^-(aq)$$

It turns blue litmus red. It forms salts with metallic oxides, hydroxides, carbonates and bicarbonates giving only one series of salts called **nitrates**.

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$

$$NaHCO_3 + HNO_3 \longrightarrow NaNO_3 + H_2O + CO_2$$

$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$

2. Decomposition. Nitric acid decomposes on heating giving nitrogen dioxide, water and oxygen.

$$4HNO_3(aq) \xrightarrow{Heat} 4NO_2(g) + O_2(g) + 2H_2O(l)$$

3. Action on metals. With the exception of gold and platinum (noble metals), nitric acid attacks all metals forming a variety of products. The product depends upon the *nature of metal, the concentration of acid and temperature*.

A. Metals that are more electropositive than hydrogen (Mg, Al, Mn, Zn, Fe, Pb, etc.). *In this case nascent hydrogen is liberated which further reduces nitric acid.*

$$\underset{(Metal)}{M} + 2HNO_3 \longrightarrow M(NO_3)_2 + 2H$$

$$HNO_3 + H \longrightarrow \text{Reduction product} + H_2O$$

In this case, the principal product is NO_2 with conc. HNO_3, N_2O with dil. HNO_3 and ammonium nitrate with very dil. HNO_3. For example, Zn reacts as:

Using concentrated nitric acid (forms nitrogen dioxide)

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H$$

$$HNO_3 + H \longrightarrow NO_2 + H_2O] \times 2$$

$$Zn + 4HNO_3 \longrightarrow \underset{\text{Nitrogen dioxide}}{Zn(NO_3)_2} + 2NO_2 + 2H_2O$$

(Conc.)

Using dilute nitric acid (forms nitrous oxide)

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$

$$2HNO_3 + 8H \longrightarrow 5H_2O + N_2O$$

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + \underset{\text{Nitrous oxide}}{N_2O} + 5H_2O$$

(Dilute)

Using very dilute nitric acid (forms ammonium nitrate)

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$

$$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + \underset{\text{Ammonium nitrate}}{NH_4NO_3} + 3H_2O$$

(V. dilute)

B. Metals which are less electropositive than hydrogen (Cu, Bi, Hg, Ag). In this case *nascent hydrogen is not liberated.*

$$HNO_3 \longrightarrow \text{Reduction product} + H_2O + [O]$$

$$\text{Metal} + (O) + HNO_3 \longrightarrow \text{Metal nitrate} + H_2O$$

The principal product is NO_2 with conc. HNO_3 and NO with dil. HNO_3. For example, Cu reacts as

Using concentrated nitric acid

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + [O]$$

$$Cu + O + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

$$Cu + 4HNO_3 \longrightarrow \underset{\text{Nitrogen dioxide}}{Cu(NO_3)_2} + 2NO_2 + 2H_2O$$

(Conc.)

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Using dilute nitric acid

$$2HNO_3 \longrightarrow 2NO + H_2O + 3[O]$$
$$Cu + O + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O] \times 3$$

$$3Cu + 8HNO_3 \longrightarrow \underset{\text{Dilute}}{3Cu(NO_3)_2} + \underset{\text{Nitric oxide}}{2NO} + 4H_2O$$

Similarly,

$$Hg + 4HNO_3 \longrightarrow \underset{\text{(conc.)}}{} Hg(NO_3)_2 + 2NO_2 + 2H_2O$$
Mercuric nitrate

$$6Hg + 8HNO_3 \longrightarrow \underset{\text{(dil.)}}{} 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$
Mercurous nitrate

$$Ag + 2HNO_3 \longrightarrow \underset{\text{(conc.)}}{} AgNO_3 + NO_2 + 2H_2O$$

$$3Ag + 4HNO_3 \longrightarrow AgNO_3 + NO + 2H_2O$$
$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$$

It may be noted that some metals such a chromium and aluminium donot dissolve in conc. HNO_3 because of the formation of **a passive film of oxide** on their surfaces.

C. Action on noble metals. Noble metals like gold and platinum are not attacked by nitric acid. However, these metals are attacked by *aqua regia* (3 parts conc. HCl and 1 part conc. HNO_3) forming their chlorides.

$$\underbrace{HNO_3 + 3HCl}_{\text{Aqua regia}} \longrightarrow \underset{\text{Nitrosyl chloride}}{NOCl} + 2H_2O + 2Cl$$

The free chlorine attacks gold, platinum, etc.

$$Au + 3Cl \longrightarrow \underset{\text{Gold chloride}}{AuCl_3}$$
$$Pt + 4Cl \longrightarrow \underset{\text{Platinum chloride}}{PtCl_4}$$

Chemical Reaction of Metal and HNO_3

It may be noted that during chemical reactions of metals with HNO_3, it not only acts as acid but also as an oxidising agent. During its reaction, it gives a variety of reduction products. The different stages of reduction of nitric acid are:

$$\overset{+5}{HNO_3} \xrightarrow{+e^-} \overset{+4}{NO_2} \xrightarrow{+2e^-} \overset{+2}{NO} \xrightarrow{+e^-} \overset{+1}{N_2O}$$
$$\xrightarrow{+4e^-} \overset{-3}{NH_3}$$

The product of the reduction of HNO_3 depends upon the

(*i*) *nature of the metal*
(*ii*) *concentration of nitric acid*
(*iii*) *temperature.*

In general, *the more the dilution, the greater is the extent of reduction.*

The mode of reactions of HNO_3 and metals can be divided into two main categories.

(*a*) Metals lying above hydrogen in electrochemical series react with HNO_3 as:

$$\text{Metal} + HNO_3 \longrightarrow \text{Metal nitrate} + H$$
$$HNO_3 + H \longrightarrow \text{Reduction product} + H_2O$$

(*b*) Metals lying below hydrogen in electrochemical series react with HNO_3 as:

$$HNO_3 \longrightarrow \text{Reduction product} + H_2O + [O]$$
$$\text{Metal} + HNO_3 + O \longrightarrow \text{Metal nitrate} + H_2O$$

4. Oxidising nature – Oxidation of non-metals and compounds. Nitric acid behaves as a *strong oxidising agent.* It has a tendency to give nascent oxygen as :

$$2HNO_3 \underset{\text{(conc.)}}{\longrightarrow} 2NO_2 + H_2O + O$$
$$2HNO_3 \underset{\text{(dilute)}}{\longrightarrow} 2NO + H_2O + 3(O)$$

Therefore, nitric acid oxidises many non-metals and compounds.

A. Oxidation of non-metals. Dilute nitric acid has no action on non-metals like carbon, sulphur, phosphorus, etc. However, concentrated nitric acid oxidises many non-metals. For example,

(*i*) *Nitric acid oxidises sulphur to sulphuric acid*

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 3$$
$$\tfrac{1}{8}S_8 + H_2O + 3O \longrightarrow H_2SO_4$$

$$\tfrac{1}{8}S_8 + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$
$$\text{or } S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 12H_2O$$

(*ii*) *Nitric acid oxidises carbon to carbonic acid*

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 2$$
$$C + H_2O + 2O \longrightarrow H_2CO_3$$

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + 2H_2O$$

(*iii*) *Nitric acid oxidises phosphorus to phosphoric acid*

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 5$$
$$2P + 3H_2O + 5O \longrightarrow 2H_3PO_4$$

$$2P + 10HNO_3 \longrightarrow 2H_3PO_4 + 10NO_2 + 2H_2O$$
$$\text{or } P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$
$$\text{or } P_4 + 20\,HNO_3 \longrightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4} + 20\,NO_2 + 4H_2O$$

(*iv*) *It oxidises iodine to iodic acid.*

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 5$$
$$I_2 + H_2O + 5O \longrightarrow 2HIO_3$$

$$I_2 + 10HNO_3 \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10NO_2 + 4H_2O$$

(*v*) *Nitric acid oxidises arsenic to arsenic acid.*

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O] \times 5$$
$$2As + 3H_2O + 5O \longrightarrow 2H_3AsO_4$$

$$2\,As + 10HNO_3 \longrightarrow 10NO_2 + 2H_3AsO_4 + 2H_2O$$
$$\text{or } As + 5HNO_3 \longrightarrow 5NO_2 + \underset{\text{Arsenic acid}}{H_3AsO_4} + H_2O$$

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Similarly,

$$Sb + 5HNO_3 \longrightarrow \underset{\text{Antimonic acid}}{H_3SbO_4} + H_2O + 5NO_2$$

Nitrous acid versus nitric acid Although nitric acid acts only as an oxidising agent, nitrous acid acts both as an oxidising agent as well as reducing agent.

- HNO_2 can be easily oxidised to HNO_3, therefore, it acts as a reducing agent.

  e.g., $HNO_2 + I_2 + H_2O \longrightarrow 2HI + HNO_3$

- HNO_2 can be easily reduced to NO, therefore, it acts as an oxidising agent.

  e.g., $H_2S + 2HNO_2 \longrightarrow 2H_2O + 2NO + S$

  $2KI + 2HNO_2 \longrightarrow 2KOH + I_2 + 2NO$

  $SO_2 + 2HNO_2 \longrightarrow H_2SO_4 + 2NO$

B. Oxidation of compounds. Dilute as well as concentrated nitric acid oxidises a number of compounds.

(*vi*) *Nitric acid oxidises hydrogen sulphide to sulphur.*

dil HNO_3 :

$$3H_2S + 2HNO_3 \longrightarrow 2NO + 4H_2O + 3S$$

conc. HNO_3 :

$$H_2S + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + S$$

(*vii*) *Nitric acid oxidises sulphur dioxide to sulphuric acid*

dil HNO_3 :

$$3SO_2 + 2HNO_3 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO$$

conc. HNO_3 :

$$SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$$

(*viii*) *Nitric acid oxidises ferrous sulphate to ferric sulphate.*

dil HNO_3 :

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

conc. HNO_3 :

$$2FeSO_4 + 2HNO_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO_2 + 2H_2O$$

5. Action on organic compounds. Nitric acid also reacts with organic compounds. For example, sucrose (cane sugar) is oxidised to oxalic acid by nitric acid.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 36HNO_3 \longrightarrow 6\ \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} + 36NO_2 + 23H_2O$$

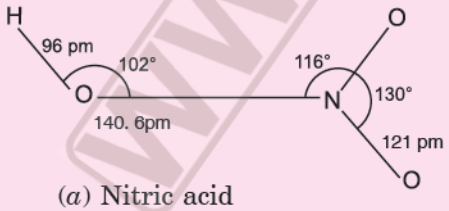
In the presence of sulphuric acid, nitric acid reacts with aromatic compounds forming nitro compounds. This process is called **nitration.** For example, it reacts with benzene to form nitrobenzene.

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

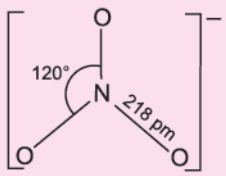
Similarly, phenol reacts with nitric acid in the presence of H_2SO_4 to give 2, 4, 6-trinitrophenol (known as picric acid).

Nitric acid attacks proteins giving a yellow nitro compound known as *xantho protein*. Therefore, nitric acid stains skin and renders wool yellow.

Structure. Spectroscopic studies have shown that gaseous nitric acid has planar structure [Fig. 9 (*a*)]. Nitrate ion, NO_3^- has also planar symmetrical structure [Fig. 9 (*b*)].



(*a*) Nitric acid



(*b*) Nitrate ion

The structure of NO_3^- is resonance hybrid of the following structures :

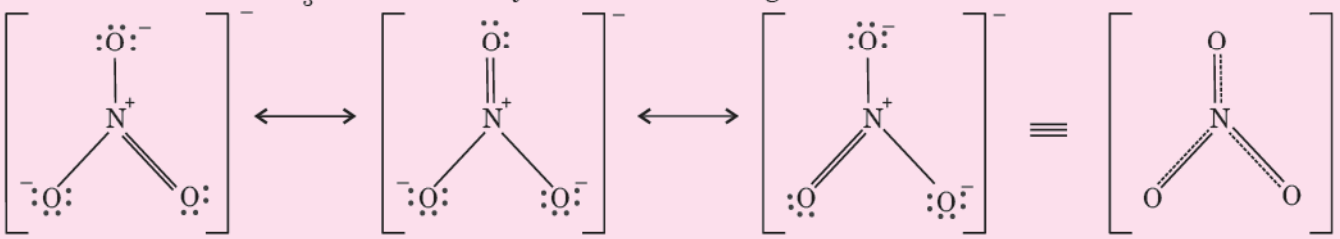


Fig. 9. Structure of nitric acid and nitrate ion

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Brown Ring test for NO_3^- ion

Nitrates give brown ring test with Fe^{2+} ions in the presence of conc. H_2SO_4. This is based upon the tendency of Fe^{2+} to reduce nitrates to nitric oxide which reacts with Fe^{2+} to form a brown coloured complex during the qualitative test for nitrates. The test is usually performed by adding dilute $FeSO_4$ solution to an aqueous solution containing NO_3^- ion and then adding conc. H_2SO_4 slowly along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid indicates the presence of NO_3^- ion.

$$3Fe^{2+} + NO_3^- + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$Fe^{2+} + NO + 5H_2O \longrightarrow \underset{\text{(Brown complex)}}{[Fe(H_2O)_5\,NO]^{2+}}$$

The colour of the complex, $[Fe(H_2O)_5NO]^{2+}$ is due to **charge transfer** *i.e.*, an electron is transferred from NO to Fe^{2+} ion. As a result, this complex formally contains Fe (+1) and NO^+ (nitrosonium ion). The complex is named as pentaaquanitrosonium iron (I) (and not as pentaaquanitrosyl iron (II) ion.

Uses of Nitric Acid

(*i*) It is used in the manufacture of ammonium nitrate for fertilizers.
(*ii*) It is used in the manufacture of sulphuric acid by lead chamber process.
(*iii*) It is used in the manufacture of explosives such as trinitro toluene (TNT), nitroglycerine, picric acid, etc.
(*iv*) It is used in the manufacture of dyes, perfumes and silk.
(*v*) It is used for the manufacture of nitrates for use in explosive and pyrotechnics.
(*vi*) It is used in pickling (cleaning) of stainless steel and etching of metals.
(*vii*) It is also used as an oxidizer in rocket fuels.
(*viii*) It is used in the purification of gold and silver as aqua regia.

SOLVED EXAMPLES

Example 7.

Why does NO_2 dimerise ? Explain.

N.C.E.R.T. *(D.S.B. 2010)(A.I.S.B. 2014, Hr. S.B. 2015, Assam S.B. 2017)*

Solution : NO_2 contains odd number of valence electrons. It behaves as a typical molecule. In the liquid and solid state, it dimerises to form stable N_2O_4 molecule, with even number of electrons. Therefore, NO_2 is paramagnetic, while N_2O_4 is diamagnetic in which two unpaired electrons get paired.

Example 8.

Ammonia is a good complexing agent. Explain. *(Pb. S.B. 2013)*

Solution : Ammonia is a good complexing agent because of the presence of lone pair of electrons on nitrogen. This lone pair can easily be donated to electron deficient compounds forming complexes. For example, it reacts with Cu^{2+} ion to form a deep blue complex.

$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow \underset{\text{Complex (deep blue)}}{[Cu(NH_3)_4]^{2+}}$$

Example 9.

Why does ammonia act as a Lewis base?

N.C.E.R.T. *(A.I.S.B. 2014 Kerala S.B. 2016, Assam S.B. 2017))*

Solution : Nitrogen atom in NH_3 has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

Example 10.

Write the products of the following reactions (give balanced chemical equations) :

(i) $Mg_3N_2 + H_2O \longrightarrow$ *(ii)* $I_2 + HNO_3$ *(conc.)* $\longrightarrow$
(iii) $Cu + HNO_3$ *(conc.)* $\longrightarrow$ *(iv)* $Li + N_2 \longrightarrow$

Solution :

(*i*) $Mg_3N_2 + 6H_2O \longrightarrow \underset{\text{Ammonia}}{3Mg(OH)_2} + 2NH_3$

(*ii*) $I_2 + 10HNO_3\ \text{(conc.)} \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + \underset{\text{Nitrogen dioxide}}{10NO_2} + 4H_2O$

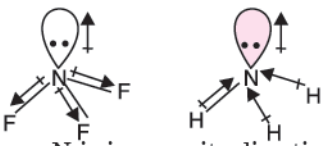
(*iii*) $Cu + 4HNO_3\ \text{(conc.)} \longrightarrow \underset{\text{Copper nitrate}}{Cu(NO_3)_2} + 2NO_2 + 2H_2O$

(*iv*) $6Li + N_2 \longrightarrow \underset{\text{Lithium nitride}}{2Li_3N}$

Example 11.

NF_3 does not have donor properties like ammonia. Explain. *(Pb. S.B. 2015)*

Solution : NF_3 has a pyramidal shape with one lone pair on N atom.



The lone pair on N is in opposite direction to the N–F bond moments and therefore, it has very low dipole moment (about 0.234 D). Thus, it does not show donor properties. But ammonia has high dipole moment because its lone pair is in the same direction as the N—H bond moments. Thus, it has donor properties.

Example 12.

Give one reaction in which ammonia acts as a reducing agent.

Solution : When ammonia is passed over heated cupric oxide, copper is formed as :

$$3CuO + 2NH_3 \xrightarrow{\text{Heat}} 3Cu + N_2 + 3H_2O$$

Example 13.

Complete the reactions :

(i) $NH_4NO_3\ (s) \xrightarrow{\text{Heat}}$
(ii) $N_2O + NaNH_2 \longrightarrow$
(iii) $Cu^{2+}(aq) + NH_3\ (aq.) \longrightarrow$
(iv) $CuO + NH_3 \longrightarrow$

Solution :

(*i*) $NH_4NO_3\ (s) \xrightarrow{\text{Heat}} N_2O\ (g) + 2H_2O\ (l)$

(*ii*) $N_2O + 2NaNH_2 \longrightarrow NaN_3 + NH_3 + NaOH$

(*iii*) $Cu^{2+}(aq) + 4NH_3\ (aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq)$

(*iv*) $3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$

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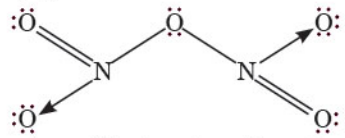
❑ **Example 14.**

What is the covalence of nitrogen in N_2O_5.

N.C.E.R.T. *(D.S.B. 2013)*

Solution : N_2O_5 has the structure



In this structure, N atom has four shared pair of electrons, two with an oxygen atom to form N = O bond, one with oxygen atom to form N–O bond and one with another oxygen atom to form N → O bond. Thus, the covalency of N in N_2O_5 is **four**. It may be noted that for a coordinate bond, the covalency is also one.

Practice Problems

6. Give an example of compounds in which the oxidation state of nitrogen is (*i*) +3 (*ii*) –3 (*iii*) 0 (*iv*) +5

7. What does the abbreviation T.N.T. stand for ?

8. What is laughing gas ? How is it prepared ?

9. Which plants mostly help in nitrogen fixing ?

10. Write the formula of the compound formed during ring test of nitrate radical. Give its name.

11. Name the oxide of nitrogen
(*i*) Which is blue solid ?
(*ii*) Causes pollution problem.

12. Which oxide of nitrogen is produced by heating lead nitrate ?

Answers to Practice Problems

1. (*i*) NF_3 (*ii*) NH_3 (*iii*) N_2 (*iv*) N_2O_5

7. Trinitrotoluene

8. N_2O. It is prepared by heating ammonium nitrate.

9. Leguminous plants

10. $[Fe(H_2O)_5NO]SO_4$.
pentaaquanitrosoniumiron(I) sulphate

11. (*i*) N_2O_3 (*ii*) NO

12. NO_2

CHEMISTRY OF PHOSPHORUS AND ITS COMPOUNDS

PHOSPHORUS

We have already learnt that phosphorus is widely distributed in nature. It occurs mainly in the form of phosphate minerals in the crust of earth.

Phosphorus is produced by heating bone ash (containing about 58% of calcium phosphate) or phosphate rock [Phosphorite, $Ca_3(PO_4)_2$] with silica (SiO_2) and coke in an electric furnace at 1775 K.

The reactions taking place are :

$$2Ca_3(PO_4)_2 + 6SiO_2 \xrightarrow{1775\ K} \underset{\text{Calcium silicate}}{6CaSiO_3} + P_4O_{10}$$

$$P_4O_{10} + 10C \xrightarrow{1775\ K} 10CO + P_4$$

The vapour of phosphorus thus produced upon condensation give white phosphorus, which exists as P_4.

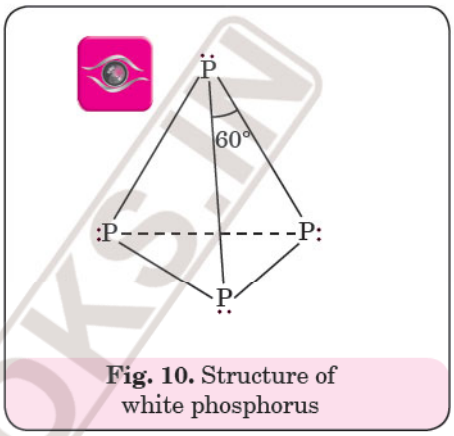


Fig. 10. Structure of white phosphorus

ALLOTROPIC FORMS OF PHOSPHORUS

Phosphorus exists in many allotropic forms. Of these three main allotropic forms are :

(*i*) *White phosphorus*
(*ii*) *Red phosphorus*
(*iii*) *Black phosphorus*

1. White phosphorus. It is the common variety of phosphorus and is obtained from phosphorite rock with coke and sand in an electric furnace at 1775 K as explained above. It consists of P_4 units as shown in Fig. 10. In this case, the four P-atoms lie at the corners of a regular tetrahedron with ∠PPP = 60°. Each phosphorus is bonded to each of the other three P-atoms by covalent bonds, so that each P-atom completes its valence shell.

Properties :

The main characteristics of white phosphorus are :

(*i*) It is soft, translucent white waxy solid with garlic smell.

(*ii*) It can be cut with a knife.

(*iii*) It melts at 317 K and boils at 553 K.

(*iv*) It is insoluble in water but soluble in benzene, carbon disulphide, liquid NH_3.

(*v*) It is very poisonous. The vapours of phosphorus, if continuously inhaled, may prove fatal.

(*vi*) It glows in dark (a property known as *chemiluminescence).*

(*vii*) White phosphorus, P_4 molecule are stable upto 1070 K even in the vapour phase. When heated above 1070 K, P_4 molecules begin to dissociate into P_2 molecules which have a bond enthalpy of 489.6 kJ mol^{-1}.

$$P_4 \underset{}{\overset{\text{above } 1070\ K}{\rightleftharpoons}} 2P_2$$

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(*viii*) White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions. This is because of angular strain in the P_4 molecules where the angles are only 60°. Its ignition temperature is very low (303 K) and therefore, it catches fire in air to form dense white fumes of P_4O_{10}. Therefore, it cannot be kept in air to form dense white fumes of P_4O_{10}. It is generally stored under water.

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

(*ix*) It combines with metals forming their phosphides such as Na_3P, Mg_3P_2, Ca_3P_2, Ag_3P, Cu_3P_2, etc.

$$12Na + P_4 \longrightarrow \underset{\text{Sodium phosphide}}{4Na_3P}$$

$$12Ag + P_4 \longrightarrow \underset{\text{Silver phosphide}}{4Ag_3P}$$

$$6Mg + P_4 \longrightarrow \underset{\text{Magnesium phosphide}}{2Mg_3P_2}$$

The reaction with sodium or potassium is very vigorous.

(*x*) It is a weak reducing agent and reduces sulphuric acid to sulphur dioxide, nitric acid to nitrogen peroxide, etc.

$$P_4 + 10H_2SO_4 \longrightarrow 10SO_2 + \underset{\text{Phosphoric acid}}{4H_3PO_4} + 4H_2O$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

It also reduces solutions of copper, silver and gold salts to their corresponding metals.

$$P_4 + 3\underset{\text{Copper sulphate}}{CuSO_4} + 6H_2O \longrightarrow Cu_3P_2 + 2H_3PO_3 + 3H_2SO_4$$

$$Cu_3P_2 + 5CuSO_4 + 8H_2O \longrightarrow 8Cu + 5H_2SO_4 + 2H_3PO_4$$

$$\text{or } P_4 + 8CuSO_4 + 14H_2O \longrightarrow 8Cu + 8H_2SO_4 + 2H_3PO_4 + 2H_3PO_3$$

Similarly,

$$P_4 + 20AgNO_3 + 16H_2O \longrightarrow 20Ag + 4H_3PO_4 + 20HNO_3$$

(*xi*) It readily combines with halogens to form trihalides (PX_3) and on prolonged treatment forms pentahalides (PX_5). For example, white phosphorus catches fire in chlorine forming phosphorus trichloride (PCl_3) and phosphorus pentachloride (PCl_5).

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

$$P_4 + \underset{\text{(excess)}}{10Cl_2} \longrightarrow 4PCl_5$$

(*xii*) White phosphorus combines with sulphur with explosive violence forming a number of sulphides such as P_2S_3, P_2S_5, P_4S_3, P_4S_7, etc.

$$8P_4 + 3S_8 \longrightarrow \underset{\text{Tetraphosphorus trisulphide}}{8P_4S_3}$$

(*xiii*) On heating with caustic soda solution, it forms phosphine.

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sodium hypophosphite}}{NaH_2PO_2}$$

This is an example of *disproportionation reaction* in which oxidation state of phosphorus decreases from 0 in P_4 to –3 in PH_3, while it increases from 0 in P_4 to +1 in NaH_2PO_4.

Strike anywhere matches

The sulphide, P_4S_3 is used in ***strike anywhere matches***. The matches contain P_4S_3, $KClO_3$, fillers and gelatin as a binder. The frictional heat between the match stick and the sand paper on the side of the match box initiates a violent reaction between P_4S_3 and $KClO_3$. This generates sufficient heat which makes match stick to burst into flames.

2. Red phosphorus. It is obtained by heating white phosphorus in an inert atmosphere (out of contact of air) at 573 K for several days.

$$\underset{\text{White phosphorus}}{P_4(s)} \xrightarrow[\text{inert atmosphere}]{573\ K} \underset{\text{Red phosphorus}}{P_4\,(s)}$$

Like white phosphorus, red phosphorus also exists as P_4 tetrahedra but have polymeric structure consisting of P_4 tetrahedra linked together as shown in Fig 11.

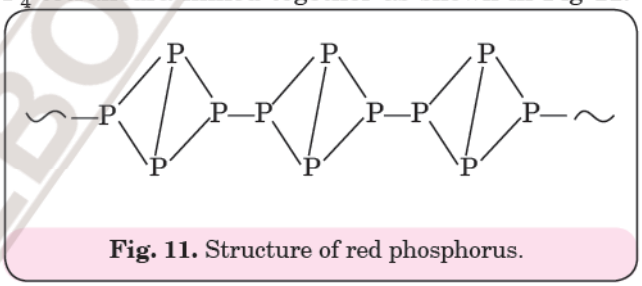

Fig. 11. Structure of red phosphorus.

In this structure, P_4 molecules are linked by covalent bonds. The important **characteristics** of red phosphorus are :

(*i*) It is a hard crystalline solid without any smell. It posesses iron grey lustre.

(*ii*) It is non-poisonous in nature.

(*iii*) It is insoluble in water as well as carbon disulphide.

(*iv*) It is denser than white phosphorus.

(*v*) It does not glow in the dark.

(*vi*) Red phosphorus is quite stable and its ignition temperature is quite high (543 K). It, therefore, does not catch fire easily.

(*vii*) Chemically it is less reactive than white phosphorus.

(*viii*) It is a bad conductor of electricity.

(*ix*) It burns with oxygen at 565 K to form phosphorus pentoxide.

$$P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s)$$

(*x*) Being less reactive than white phosphorus, it reacts with halogens, sulphur and alkali metals only when heated forming their corresponding salts.

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$$P_4 + 6Cl_2 \xrightarrow{Heat} 4PCl_3$$

$$P_4 + 10Cl_2 \xrightarrow{Heat} 4PCl_5$$

$$4P_4 + 3S_8 \xrightarrow{Heat} 8P_2S_3$$

$$P_4 + 12Na \xrightarrow{Heat} 4Na_3P$$

(*xi*) Red phosphorus does not react with caustic alkalies. This property is made use in separating red phosphorus from white phosphorus.

(*xii*) Red phosphorus can be converted into white phosphorus by boiling it in an inert atmosphere and then condensing the vapours of white phosphorus formed under water.

3. Black phosphorus. Black phosphorus has two forms; α-black phosphorus and β-black phosphorus, α-black phosphorus is formed by heating red phosphorus in a sealed tube at 803 K.

$$\text{Red phosphorus} \xrightarrow[\text{sealed tube}]{803\ K} \alpha\text{-Black phosphorus}$$

It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.

β-Black phosphorus is obtained by heating white phosphorus at 473 K under very high pressure (4000–12000 atm) in an inert atmosphere.

$$\text{White phosphorus} \xrightarrow[4000-1200\ \text{atm. pressure}]{473\ K} \beta\text{-Black phosphorus}$$

It has a double layered crystal lattice. Each layer is made up of zig-zag chains with P—P—P bond angles of 99° (Fig. 12) and P—P bond distance of 218 pm . Since it is highly polymeric, therefore, it has high density.

The important characteristics of black phosphorus are :

(*i*) It has a black metallic lustre.

(*ii*) It has sharp melting point of 860 K. Its specific gravity is 2.69.

(*iii*) It has a highly polymeric layered structure and exists in three crystalline and one amorphous forms. Therefore, it has high density.

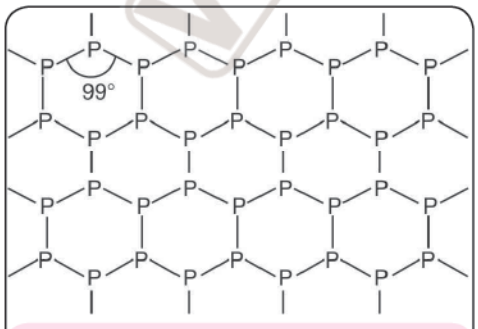

Fig. 12. Structure of black phosphorus.

(*iv*) It is a moderate conductor of heat and electricity.

(*v*) It is thermodynamically the most stable and inactive form of phosphorus. It does not burn in air upto 673 K.

Thus, the three allotropes of phosphorus differ in their chemical reactivity. **White phosphorus is the most reactive form while black phosphorus is the least reactive form.** Therefore, white phosphorus is stored under water to protect it from air while red and black phosphorus are stable in air.

REMEMBER

- White P is most reactive form
  while
- Black P is the least reactive form.

The main characteristics of three forms of phosphorus are summed up in Table 7.

Table 7. Some physical properties of three forms of phosphorus.

Properties	White phosphorus	Red phosphorus	Black phosphorus
Colour	White but turns yellow on exposure	Dark red	Black
State	Waxy solid	Brittle powder	Crystalline
Density	1.84 g cm^{-3}	2.1 g cm^{-3}	2.69 g cm^{-3}
Ignition temperature	307 K	543 K	673 K
Stability	Less stable at ordinary temperature	More stable at ordinary temperature	Most stable
Chemical reactivity	Very reactive	Less reactive	Least reactive

Phosphatic Fertilizers

To increase the fertility of soil certain chemical compounds known as **fertilizers** are used. These provide the essential nutrients, potassium, nitrogen and phosphorus. The most important phosphatic fertilizer is superphosphate of lime $Ca(H_2PO_4)_2$. This is produced directly from phosphate rocks by treatment with H_2SO_4. This makes insoluble phosphate rock soluble in water to improve the release of phosphorus to the soil for uptake by plants.

$$Ca_3(PO_4)_2 + 2H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

The phosphatic rock generally contains fluorides which react with H_2SO_4 to give HF which in turn forms other side products. The gaseous side products are removed by washing with water in a scrubber. About 90% of phosphate rock mined is used for the production of phosphatic fertilizers and the remaining 10% is used for the production of elemental phosphorus. Treatment of phosphate rock with phosphoric acid gives triple super phosphate, $Ca(H_2PO_4).H_2O$. It is free from calcium sulphate and therefore, contains larger percentage of phosphorus :

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$Ca_5(PO_4)_3F + 7H_3PO_4 + 5H_2O \longrightarrow 5Ca(H_2PO_4)_2.H_2O + HF$

Phosphate Esters

Phosphate esters are important in life processes. The most important of these biomolecules are DNA, RNA, adenosine *mono-*, *di-* and *tri*-phosphates (AMP, ADP and ATP). These are discussed in Unit 14. These contains P-O-P links, the hydrolysis of these links releases energy which can be put to useful work.

PHOSPHINE

It is hydride of phophorus, PH_3.

Preparation

(*i*) **From phosphides.** By the action of water or dilute mineral acid on metallic phosphides (Ca_3P_2, AlP, etc.)

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

Calcium phosphide

$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$

Calcium phosphide

$$AlP + 3HCl \longrightarrow AlCl_3 + PH_3$$

Aluminium phosphide

(*ii*) **From phosphorous acid.** Pure phosphine can be prepared by heating phosphorous acid at 478 – 483 K.

$$4H_3PO_3 \xrightarrow{478-483K} 3H_3PO_4 + PH_3$$

Phosphorous acid — Phosphoric acid

(*iii*) **From phosphonium salts.** Pure phosphine can also be obtained by heating phosphonium iodide with caustic soda solution.

$$PH_4I + NaOH \longrightarrow NaI + H_2O + PH_3$$

Phosphonium iodide is obtained from phosphorus.

$$P_4 + 2I_2 + 8H_2O \longrightarrow 2PH_4I + 2HI + 2H_3PO_4$$

(*iv*) **Laboratory preparation.** Phosphine is prepared in the laboratory by heating white phosphorus with concentrated sodium hydroxide solution in an inert atmosphere of carbon dioxide or coal gas.

$$4P + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

Sodium hypophosphite

It may be noted that pure phosphine is not inflammable but the gas may catch fire in air. This may be due to the presence of impurity of P_2H_4 which is spontaneously inflammable. Therefore, a current of carbon dioxide, coal gas is passed through the flask to displace air.

To get pure phosphine, the gas is passed through a U-tube placed in a freezing mixture. The liquid P_2H_4 gets condensed while PH_3 remains unaffected. Impure gas may also be purified by treating it with hydrogen iodide followed by heating with KOH solution.

$$PH_3 + HI \longrightarrow PH_4I$$

Phosphonium iodide

$$PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$$

The impurity P_2H_4 may also be controlled by using alcoholic solution of potassium hydroxide in place of aqueous solution of caustic soda.

Structure

Like ammonia, phosphine has pyramidal structure. Phosphorus involves sp^3 hybridisation. Three bonds are formed by the overlap of sp^3 hybrid orbitals of phosphorus with 1*s*-orbital of hydrogen. One of the orbital is occupied by a lone pair of electrons. The HPH bond angle in PH_3 is 93.6° and P—H bond distance 142 pm.

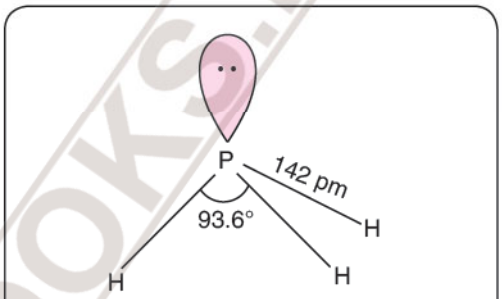

Fig. 13. Structure of phosphine

PROPERTIES OF PHOSPHINE

Physical properties

(*i*) It is a colourless gas with unpleasant smell of rotten fish or garlic.

(*ii*) It is highly poisonous in nature.

(*iii*) It is heavier than air (vapour density = 17) and is slightly soluble in water.

(*iv*) On cooling to 185.5 K, phosphine condenses to a liquid and on cooling to 139.5 K, it solidifies.

(*v*) It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and hydrogen.

Chemical properties

1. Action towards litmus. It is feebly basic and reacts with halogen acids to form a phosphonium salt (basic nature).

$$PH_3 + HX \longrightarrow PH^+_4X^- \quad (X = Cl, Br, I)$$

Phosphonium halide

e.g. $PH_3 + HCl \longrightarrow PH_4Cl$

Phosphonium chloride

$PH_3 + HBr \longrightarrow PH_4Br$

Phosphonium bromide

$PH_3 + HI \longrightarrow PH_4I$

Phosphonium iodide

2. Combustibility. Pure phosphine is not combustible. But when heated to 423 K in air or oxygen, it burns forming phosphoric acid.

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$$PH_3 + 2O_2 \xrightarrow{423\ K} H_3PO_4$$

3. Decomposition. By heating in the absence of air at 713 K or by passing an electric spark through it, phosphine breaks into its elements.

$$4PH_3 \xrightarrow[\text{absence of air}]{713\ K} P_4 + 6H_2$$

4. Action with chlorine. When heated in the atmosphere of chlorine, phosphine burns forming phosphorus trichloride (PCl_3) or pentachloride (PCl_5).

$$PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$$
$$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$$

5. Action with nitrous oxide. When sparked with nitrous oxide, it reduces the latter to nitrogen.

$$PH_3 + 4N_2O \longrightarrow H_3PO_4 + 4N_2$$

6. Action with nitric oxide. Nitric oxide is reduced to nitrogen.

$$PH_3 + 4NO \longrightarrow H_3PO_4 + 2N_2$$

7. Precipitation reactions. When bubbled through certain metallic salt solutions, phosphides of the metals get precipitated.

$$\underset{\text{Copper sulphate}}{3CuSO_4} + 2PH_3 \longrightarrow \underset{\substack{\text{Cupric phosphide}\\(\text{Black ppt.})}}{Cu_3P_2} + 3H_2SO_4$$

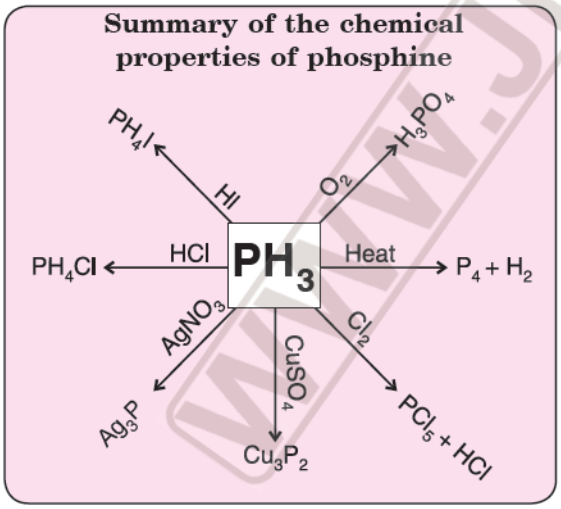
$$\underset{\text{Mercuric chloride}}{3HgCl_2} + 2PH_3 \longrightarrow \underset{\text{Mercuric phosphide}}{Hg_3P_2} + 6HCl$$

$$\underset{\text{Silver nitrate}}{3AgNO_3} + PH_3 \longrightarrow \underset{\substack{\text{Silver phosphide}\\(\text{Black ppt.})}}{Ag_3P} + 3HNO_3$$

Silver phosphide is converted to silver as follows:

$$Ag_3P + 3AgNO_3 + 3H_2O \longrightarrow 6Ag + 3HNO_3 + H_3PO_3$$

Summary of the chemical properties of phosphine



Uses of Phosphine

(*i*) It is used in preparing **Holme's signals** for the ships to know about the position of the rocks in the sea.

REMEMBER

Holme's signals give signals to ships in deep seas and oceans about danger points.

A mixture of calcium carbide and calcium phosphide is taken in a vessel. A hole is made in it and the vessel is immersed in the sea water near the rock. While calcium phosphide liberates phosphine and calcium carbide liberates acetylene.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

Phosphine catches fire in air and lights up acetylene. This acts as a signal for the approaching ship.

(*ii*) It is used to prepare **Smoke screens** in warfare. **Calcium phosphide** reacts with water to form phosphine which burns in air to form P_4O_{10} which acts as a smoke screen.

Comparision between Phosphine and Ammonia

Both ammonia and phosphine are the hydrides of the **elements N** and **P** respectively which belong to the group 15 of the periodic table.

Thus, these hydrides are expected to have many common characteristics. But they differ also in some of the properties. The comparison between the properties of ammonia and phosphine is given below.

Property	Phosphine	Ammonia
Points of resemblence		
1. Colour	Colourless	Colourless
2. Decomposition by electric spark	Decomposes into elements	Decomposes into elements
3. Action with chlorine	Reacts violently to form PCl_5	Reacts with chlorine to form nitrogen trichloride
4. Actions with halogen acids	Forms phosphonium salts	Forms ammonium salts
5. Combustibility	Burns in air to form phosphoric acid	Burns in air to form nitrogen and water
Points of differences		
1. Smell	Unpleasant smell of rotten fish.	Characteristic ammoniacal
2. Density	Heavier than air.	smell.
3. Solubility	Sparingly soluble in water.	Highly soluble in water.
4. Nature	Highly poisonous.	Non-poisonous.
5. Action towards	Neutral.	Basic.
6. Stability	Less stable.	More stable.
7. Stability of salts	Less stable.	More stable.

HALIDES OF PHOSPHORUS

Phosphorus forms two types of halides *i.e.*, phosphorus trihalides (covalency of P = 3) PX_3(X = F, Cl, Br, I) and phosphorus pentahalides PX_5(X = F, Cl, Br) (covalency of P = 5). With chlorine it forms :

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1. Phosphorus trichloride
2. Phosphorus pentachloride.

1. Phosphorus trichloride, PCl_3

Preparation. It is prepared in the laboratory by passing dry chlorine gas over heated white phosphorus. The vapours of PCl_3 distil over and are collected in a receiver cooled by water.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

The receiver has a calcium chloride tube attached to it which protects it from the reactions of outside moisture. It can be purified by distilling over white phosphorus to remove the excess of chlorine.

It can also be obtained by the reaction of thionyl chloride with white phosphorus

$$P_4 + \underset{\text{Thionyl chloride}}{8SOCl_2} \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Structure

Phosphorus in PCl_3 undergoes sp^3 hybridisation. Three of the sp^3 hybrid orbitals overlap with p-orbitals of chlorine to form three P—Cl σ bonds while the fourth sp^3 hybrid orbital contains a lone pair of electrons. Therefore, like PH_3, PCl_3 has pyramidal structure as shown in Fig. 14.

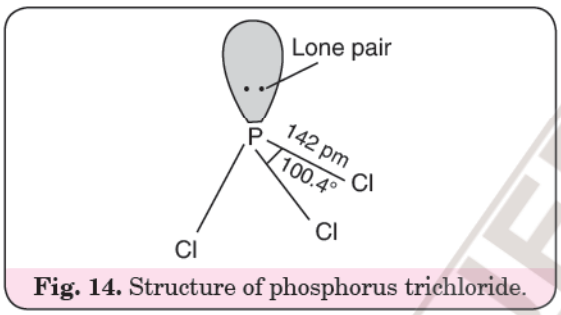

Fig. 14. Structure of phosphorus trichloride.

The Cl—P—Cl bond angle in PCl_3 is 100.4° which is greater than HPH bond angle in PH_3(93.6°). This is due to stearic crowding of two large Cl atoms in comparison to H atoms. As expected the P—Cl bond is much larger (240 pm) than P—H bond (142 pm) because of larger size of Cl atom.

Properties of Phosphorus Trichloride

Physical Properties

(*i*) It is a colourless oily liquid fuming constantly is the moist air.
(*ii*) Its specific gravity is 1.6.
(*iii*) Its boiling point and freezing point values are 347 K and 161 K respectively.
(*iv*) It has a highly pungent smell.

Chemical properties

1. Action with water. It fumes in moist air and reacts with water violently to form phosphorous acid.

$$PCl_3 + 3H_2O \longrightarrow \underset{\text{Phosphorous acid}}{H_3PO_3} + 3HCl$$

2. Action with atmospheric air or oxygen. It slowly combines with dry oxygen to form phosphorus oxychloride.

$$2PCl_3 + O_2 \longrightarrow \underset{\text{Phosphorous oxychloride}}{2POCl_3}$$

3. Action with sulphur trioxide. It reacts with sulphur trioxide to form phosphorus oxychloride.

$$PCl_3 + SO_3 \longrightarrow \underset{\text{oxychloride}}{\overset{\text{Phosphorus}}{POCl_3}} + SO_2$$

4. Action with chlorine or sulphur. It combines with chlorine or sulphur to form phosphorus pentachloride or thiophosphorus oxychloride.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$
$$PCl_3 + S \longrightarrow \underset{\text{Thiophosphorus oxychloride}}{PSCl_3}$$

5. Action with sulphur monochloride, thionyl chloride and sulphuryl chloride. It is readily oxidised to phosphorus (V) derivatives, PCl_5, $POCl_3$ and $PSCl_3$.

$$3PCl_3 + \underset{\text{monochloride}}{\overset{\text{Sulphur}}{S_2Cl_2}} \longrightarrow PCl_5 + 2PSCl_3$$

$$3PCl_3 + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow POCl_3 + PSCl_3 + PCl_5$$

$$PCl_3 + \underset{\text{Sulphuryl chloride}}{SO_2Cl_2} \longrightarrow PCl_5 + SO_2$$

In these reactions, PCl_3 behaves as a reducing agent.

6. Action with organic compounds. It reacts with organic compounds containing —OH group such as acetic acid, ethyl alcohol, etc.
(*i*) With organic acid, it forms acid chlorides.

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

(*ii*) With alcohols, it forms alkyl chlorides.

$$\underset{\text{Ethy alcohol}}{3C_2H_5OH} + PCl_3 \longrightarrow \underset{\text{Ethyl chloride}}{3C_2H_5Cl} + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

7. Action with finely divided metals. Finely divided metals react on heating to form metal chlorides.

$$12Ag + 4PCl_3 \xrightarrow{\text{Heat}} 12AgCl + P_4$$

$$6Na + PCl_3 \xrightarrow{\text{Heat}} 3NaCl + Na_3P$$

8. PCl_3 undergoes many substitution reactions and is main source of organophosphorus compounds.

Uses

It is mainly employed in the organic chemistry as an important reagent to replace the hydroxyl group (–OH) by chlorine atom in organic reactions.

2. Phosphorus pentachloride, PCl_5

Preparation. Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + \underset{\text{(Excess)}}{10Cl_2} \longrightarrow 4PCl_5$$

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It can also be obtained by the reaction of dry chlorine on phosphorus trichloride.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

Phosphorus pentachloride can also be prepared by the action of SO_2Cl_2 on phosphorus.

$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

Structure

In PCl_5, phosphorus undergoes sp^3d hybridisation and has **trigonal bipyramidal structure** as shown in Fig. 15.

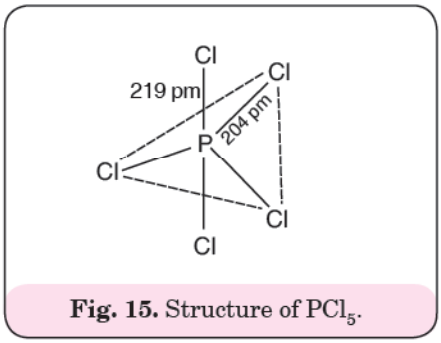

Fig. 15. Structure of PCl_5.

It has three equatorial P—Cl bonds and two axial P—Cl bonds which are different. Therefore, all the five P—Cl bonds are not equal. The axial bonds are larger than equatorial bonds as :

P—Cl (axial) = 219 pm, P—Cl (equatorial) = 204 pm

It may be noted that in gaseous and liquid phases, PCl_5 has trigonal bipyramidal structure. However, in the solid state, it exists as an ionic solid $[PCl_4]^+ [PCl_6]^-$.

In this, the cation $[PCl_4]^+$ is tetrahedral and the anion $[PCl_6]^-$ is octahedral.

In solution, it exists either molecular or ionically dissociated depending on the nature of the solvent.

Properties of Phosphorus pentachloride, PCl_5

Physical

(*i*) It is a yellowish white powder having pungent smell.

(*ii*) It fumes in moist air due to its strong affinity for water.

(*iii*) On heating, it sublimes at 433 K and can be melted (m.p. 318 K) only by heating it under pressure.

Chemical properties

1. **Stability.** PCl_5 is thermally less stable than PCl_3. On heating it sublimes but decomposes on stronger heating into trichloride and chlorine.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

2. **Action with water.** In moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \longrightarrow \underset{\text{Phosphorus oxychloride}}{POCl_3} + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow \underset{\text{Phosphoric acid}}{H_3PO_4} + 3HCl$$

3. **Action with compounds containing OH group.** It reacts with compounds containing hydroxyl groups (—OH) to give the corresponding chloro compounds in which each —OH group is replaced by a chlorine atom. For example,

(*i*) With organic acid

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

(*ii*) With ethyl alcohol

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3 + HCl$$

(*iii*) With sulphuric acid

$$\underset{\text{Sulphuric acid}}{HO—SO_2—OH} + 2PCl_5 \longrightarrow \underset{\text{Sulphuryl chloride}}{ClSO_2Cl} + 2POCl_3 + 2HCl$$

4. **Reaction with phosphorus pentoxide and sulphur dioxide.** PCl_5 reacts with P_4O_{10} forming phosphorus oxychloride and with SO_2 forming phosphorus oxychloride and thionyl chloride.

$$6PCl_5 + P_4O_{10} \longrightarrow \underset{\text{Phosphorus oxychloride}}{10POCl_3}$$

$$PCl_5 + SO_2 \longrightarrow \underset{\text{Phosphorus oxychloride}}{POCl_3} + \underset{\text{Thionyl chloride}}{SOCl_2}$$

5. **Reaction with phosphorus pentasulphide.** PCl_5 reacts with phosphorus pentasulphide to form phosphorus thiochloride.

$$6PCl_5 + \underset{\text{Phosphorus pentasulphide}}{P_4S_{10}} \longrightarrow \underset{\text{Phosphorus thiochloride}}{10PSCl_3}$$

6. **Reaction with metals.** PCl_5 reacts with finely divided metals on heating to give corresponding chlorides.

$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$
$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

7. **Reaction with chloride ion acceptors.** PCl_5 forms addition products with chloride ion acceptors such as boron trichloride containing tetrahedral $[PCl_4]^+$ species.

$$PCl_5 + BCl_3 \longrightarrow [PCl_4]^+ [BCl_4]^-$$
$$PCl_5 + NbCl_4 \longrightarrow [PCl_4]^+ [NbCl_5]^-$$

8. **Reduction.** Phosphorus pentachloride is reduced with hydrogen to form PCl_3.

$$PCl_5 + 2H \longrightarrow PCl_3 + 2HCl$$

9. **Reaction with potassium fluoride.** With KF, PCl_5 forms potassium phosphorus hexafluoride, $K^+[PF_6]^-$.

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$$PCl_5 + 6KF \longrightarrow \underset{\text{Potassium phosphorus hexafluoride}}{K^+[PF_6]^-} + 5KCl$$

Uses

It is extremely useful in organic reactions to replace a hydroxyl group (–OH) by chlorine atom such as for the synthesis of C_2H_5Cl, CH_3COCl, etc.

REMEMBER

Pentahalides are thermally less stable than trihalides. For example, PCl_5 exists as molecules in the gaseous state but exists as $[PCl_4]^+$ $[PCl_6]^-$ in the crystalline state. PBr_5 and PI_5 also exist in the ionic forms as $[PBr_4]^+$ Br^- and $[PI_4]^+I^-$ respectively in the solid state.

OXIDES OF PHOSPHORUS

Phosphorus forms two common oxides namely (*i*) *phosphorus trioxide* (P_4O_6) and (*ii*) *phosphorus pentaoxide* (P_4O_{10})

1. Phosphorus (III) oxide (P_4O_6)

Preparation

Phosphorus trioxide is formed when phosphorus is burnt in a limited supply of air.

$$P_4 + 3O_2 \text{ (limited)} \longrightarrow P_4O_6$$

Properties

(*i*) Phosphorus (III) oxide is a crystalline solid with garlic odour.

(*ii*) It is soluble in carbon disulphide, ether and chloroform.

(*iii*) **Heating in air.** On heating in air, it forms phosphorus pentaoxide.

$$P_4O_6 + 2O_2 \longrightarrow \underset{\text{Phosphorus (V) oxide}}{P_4O_{10}}$$

(*iv*) **Action of water.** It dissolves in cold water to give phosphorous acid.

$$P_4O_6 + 6H_2O \xrightarrow[\text{(cold)}]{} \underset{\text{Orthophosphorous acid}}{4H_3PO_3}$$

It is, therefore, considered as **anhydride of phosphorous acid.**

With hot water, it gives phosphoric acid and inflammable phosphine.

$$P_4O_6 + 6H_2O \text{ (hot)} \longrightarrow \underset{\text{Phosphoric acid}}{3H_3PO_4} + PH_3$$

(*v*) **Action with chlorine.** It reacts vigorously with chlorine to form a mixture of phosphoryl chloride and metaphosphoryl chloride.

$$P_4O_6 + 4Cl_2 \longrightarrow \underset{\text{Phosphoryl chloride}}{2POCl_3} + \underset{\text{Metaphosphoryl chloride}}{2PO_2Cl}$$

Structure. Each atom of phosphorus in P_4O_6 is present at the corner of a tetrahedron (just as P_4 units in elemental phosphorus). Each phosphorus atom is covalently bonded to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms. This is shown in Fig. 16. It is clear from the structure that the six oxygen atoms lie along the edges of the tetrahedron of P atoms.

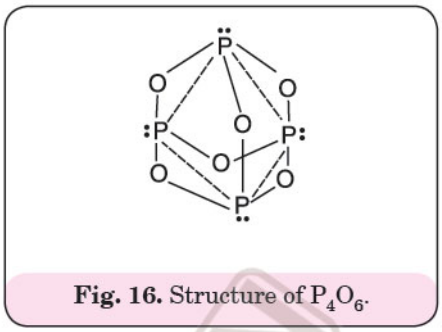

Fig. 16. Structure of P_4O_6.

2. Phosphorus (V) oxide (P_4O_{10})

Preparation

It is prepared by heating white phosphorus in excess of air.

$$P_4 + 5O_2 \text{ (excess)} \longrightarrow P_4O_{10}$$

Properties

(*i*) It is snowy white solid.

(*ii*) **Action with water.** It readily dissolves in cold water forming metaphosphoric acid

$$P_4O_{10} + 2H_2O \xrightarrow[\text{(cold)}]{} 4HPO_3$$

Metaphosphoric acid

With hot water it gives phosphoric acid.

$$P_4O_{10} + 6H_2O \xrightarrow[\text{(hot)}]{} \underset{\text{Phosphoric acid}}{4H_3PO_4}$$

(*iii*) **Dehydrating nature.** Phosphorus pentaoxide has strong affinity for water and therefore, acts as a powerful dehydrating agent. It extracts water from many organic and inorganic compounds including sulphuric acid and nitric acid.

$$H_2SO_4 \xrightarrow[-H_2O]{P_4O_{10}} SO_3$$

$$2HNO_3 \xrightarrow[-H_2O]{P_4O_{10}} N_2O_5$$

$$\underset{\text{Perchloric acid}}{2HClO_4} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Chlorine (VII) oxide}}{Cl_2O_7}$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Methyl cyanide}}{CH_3CN}$$

Structure. Its structure is similar to that of P_4O_6. In addition, each phosphorus atom forms a double bond with oxygen atom as shown in Fig. 17.

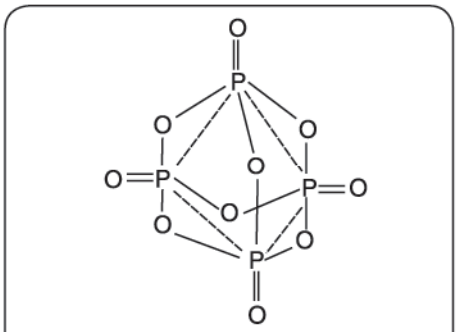

Fig. 17. Structure of P_4O_{10}.

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Phosphorus also forms phosphorus tetraoxide, P_4O_8. It is prepared from P_4O_6 as

$$4P_4O_6 \xrightarrow{440°C} \underset{\text{Red phosphorus}}{3P_4O_8} + P_4$$

It is a colourless solid.

Both P_4O_6 and P_4O_{10} are acidic oxides and they react with water to form aqueous solutions of phosphorous acid and phosphoric acid, respectively.

$$P_4O_6\,(s) + 6H_2O\,(l) \longrightarrow \underset{\text{Phosphorous acid}}{H_3PO_3\,(aq)}$$

$$P_4O_{10}\,(s) + 6H_2O\,(l) \longrightarrow \underset{\text{Phosphoric acid}}{H_3PO_4\,(aq)}$$

It readily reacts with water to give phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4).

$$P_4O_8 + 6H_2O \longrightarrow \underset{\text{Phosphorous acid}}{2H_3PO_3} + \underset{\text{Phosphoric acid}}{2H_3PO_4}$$

Its structure is similar to P_4O_6 but in addition, two P atoms form coordinate bonds with their lone pairs of electrons to two O atoms. In P_4O_{10}, all the four P atoms form coordinate bonds.

OXOACIDS OF PHOSPHORUS

Phosphorus forms a number of oxoacids as given in Table 8.

Table 8. Oxoacids of phosphorus

Name	Formula	Oxidation state of P
Phosphinic acid (or Hypophosphorous acid)	H_3PO_2	+ 1
Phosphonic acid (or orthophosphorous acid or phosphorous acid)	H_3PO_3	+ 3
Pyrophosphorous acid	$H_4P_2O_5$	+ 3
Hypophosphoric acid	$H_4P_2O_6$	+ 4
Orthophosphoric acid (or phosphoric acid)	H_3PO_4	+ 5
Diphosphoric acid (Pyrophosphoric acid)	$H_4P_2O_7$	+ 5
Metaphosphoric acid	HPO_3	+ 5
Peroxophosphoric acid	H_3PO_5	+ 5

REMEMBER

The P—OH group in oxoacids of phosphorus is ionisable and gives proton. Therefore, number of P—OH groups determines the basicity of the oxoacid.

Some important oxoacids of phosphorus are discussed below :

(*i*) Phosphinic acid or Hypophosphorous acid, H_3PO_2

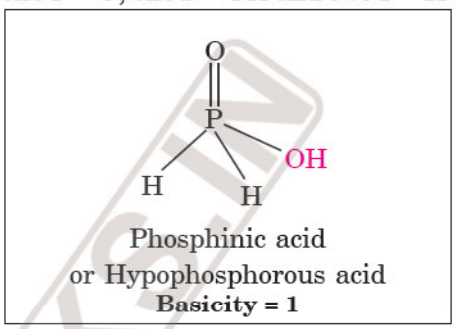
Preparation. It is prepared by heating phosphorus with alkalies like barium hydroxide when precipitate of barium phosphate is formed. The precipitate is separated and heated with a calculated amount of sulphuric acid.

$$3Ba(OH)_2 + 2P_4 + 6H_2O \xrightarrow{\text{Heat}} 2PH_3 + \underset{\text{ppt}}{3Ba(H_2PO_2)_2}$$

$$Ba(H_2PO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2H_3PO_2$$

Barium sulphate is separated by filtration and solution is concentrated when hypophosphorous acid separates out.

It has one P═O, one P—OH and two P—H bonds.



Phosphinic acid
or Hypophosphorous acid
Basicity = 1

Since it has only one P—OH bond, so it has only one ionizable hydrogen atom. Therefore, it behaves as **monobasic acid,** ionising as :

$$H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$$

The other two hydrogen atoms directly bonded to P are not ionizable. Due to the presence of two P—H bonds, the acid as well as it salt behave as **strong reducing agents.** Therefore, it is used in organic chemistry to reduce arene diazonium salts to arenes.

On heating to 313 K it decompose to phosphine

$$3H_3PO_2 \xrightarrow{315K} \underset{\text{Phosphine}}{PH_3} + \underset{\text{Phosphorous acid}}{2H_3PO_3}$$

However, on heating above 333K, it decomposes to phosphoric acid and phosphine

$$2H_3PO_2 \xrightarrow{> 333K} H_3PO_4 + \underset{\text{Phosphine}}{PH_3}$$

Phosphoric acid

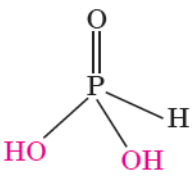
(*ii*) Orthophosphorous acid or Phosphonic acid, H_3PO_3.

Preparation. It is prepared by the hydrolysis of phosphorus trichloride or trioxide.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

It has one P═O, one P—H and two P—OH bonds.



Phosphonic acid or
Orthophosphorous acid
Basicity = 2

Since it has two P—OH bonds, so it has two ionisable H atoms. Therefore, it behaves as **dibasic** or **diprotic**:

$$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^- \quad K_{a_1} = 1 \times 10^{-2}$$

$$H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-} \quad K_{a_2} = 2 \times 10^{-7}$$

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It gives two series of salts such as NaH_2PO_3 and Na_2HPO_3, known as sodium dihydrogen phosphite and disodium hydrogen phosphite respectively.

On heating it decomposes into phosphoric acid and phosphine :

$$4H_3PO_3 \xrightarrow{457\,K} 3H_3PO_4 + PH_3$$

It is readily oxidised by air in the presence of a catalyst iodine into phosphoric acid.

$$2H_3PO_3 + O_2 \xrightarrow{Iodine} 2H_3PO_4$$

It is a strong reducing agent.

(iii) Orthophosphoric acid, H_3PO_4

Preparation. It is prepared by adding phosphorus pentaoxide to water and boiling the solution.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

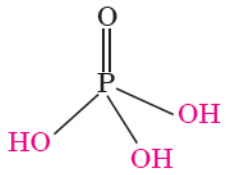
A small amount of metaphosphoric acid may also be formed but it changes readily into phosphoric acid on boiling.

It can also be prepared by heating phosphorus with conc. HNO_3 or by dissolving PCl_5 in water

$$P_4 + 20HNO_3 \xrightarrow{Heat} 4H_3PO_4 + 20NO_2 + 4H_2O$$

$$PCl_5 + 4H_2O \xrightarrow{Heat} H_3PO_4 + 5HCl$$

It has one P═O and three P—OH bonds.



Orthophosphoric acid
Basicity = 3

Since it has three P—OH bonds, so it has three ionisable H atoms. Therefore, it behaves as **tribasic** or **triprotic** and ionises in three stages :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad K_{a_1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \quad K_{a_2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \quad K_{a_3} = 1.0 \times 10^{-13}$$

Therefore, it forms three series of salts such as NaH_2PO_4 (sodium dihydrogen phosphate), Na_2HPO_4 (disodium hydrogen phosphate) and Na_3PO_4 (sodium phosphate).

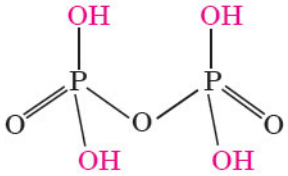
(iv) Pyrophosphoric acid, $H_4P_2O_7$

It contains phosphorus in +5 oxidation state.

Preparation. It is prepared by heating orthophosphoric acid to 523K.

$$2H_3PO_4 \xrightarrow{523\,K} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} + H_2O$$

The acid is formed by the loss of a molecule of water from two molecules of phosphoric acid and has the structure :



It contains four P—OH bonds, two P═O bonds and one P—O—P bond. Since it contains four OH groups, it is **tetrabasic.** It dissolves in water to form orthophosphoric acid.

$$H_4P_2O_7 + H_2O \xrightarrow{Heat} \underset{\text{Orthophosphoric acid}}{2H_3PO_4}$$

Upon strong heating, it decomposes to form meta phosphoric acid

$$H_4P_2O_7 \xrightarrow{873\,K} 2HPO_3 + H_2O$$

Metaphosphoric acid

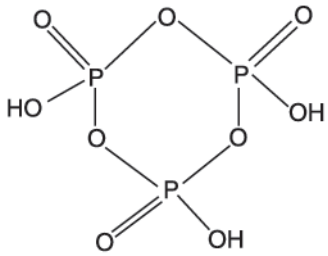
(v) Metaphosphoric acid, HPO_3

It has one P—OH bond and therefore, exists as monobasic.

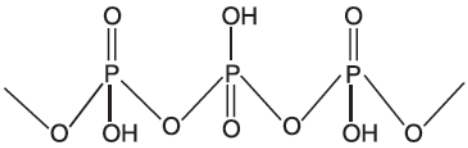
Preparation. It is prepared by heating orthophosphoric acid to 525 K.

$$\underset{\text{Orthophosphoric acid}}{H_3PO_4} \xrightarrow{525\,K} \underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O$$

However, it may be noted that metaphosphoric acid does not exist as simple monomer, rather it exists as cyclometaphosphoric acid or polymetaphosphoric acid.



Trimetaphosphoric acid
$(HPO_3)_3$



Polymetaphosphoric acid
$(HPO_3)_n$

The ***basic structural and characteristic features*** of these phosphorus oxoacids are :

(*i*) All these acids contain phosphorus atom or atoms bonded tetrahedrally to four other atoms or groups.

(*ii*) These contain at least one P═O unit and one P—OH group. The P—OH group is ionizable giving proton. The number of P—OH groups determines the basicity of the oxoacid.

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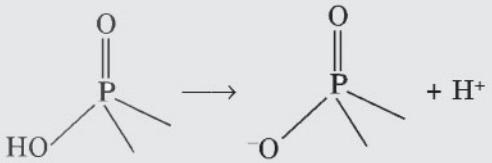
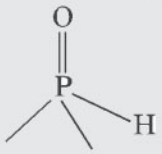
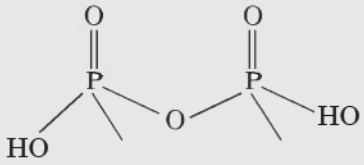


(*iii*) Some oxoacids have one (or more) P—H groups and this bond is non-ionisable.



(*iv*) Some oxoacids have P—O—P or P—P bonds obtained by corner sharing of tetrahedra.



(*v*) Peroxo acids have P—O—O—H or P—O—O—P linkages.

(*vi*) The oxoacids in which P has lower oxidation state (less than +5) contain in addition to P—OH and P=O bonds, either P—P (e.g., in $H_4P_2O_6$) or P—H (e.g., in H_3PO_2) bonds but not both. These oxoacids in +3 oxidation state of P tend to disproportionate to higher and lower oxidation states. For example, ortho phosphorous acid (or phosphorous acid) on heating disproportionates to give ortho phosphoric acid (P = +5) and phosphine, PH_3 (P = –3).

$$\underset{\text{Orthophosphorous acid}}{\overset{+3}{4H_3PO_3}} \longrightarrow \underset{\text{Orthophosphoric acid}}{\overset{+5}{3H_3PO_4}} + \underset{\text{Phosphine}}{\overset{-3}{PH_3}}$$

(*vii*) Acids which contain P—H bonds have strong reducing properties. For example, hypophosphorous acid is a good reducing agent because it contains two P—H bonds and therefore, reduces $AgNO_3$ to metallic silver.

$$4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow H_3PO_4 + 4Ag + 4HNO_3$$

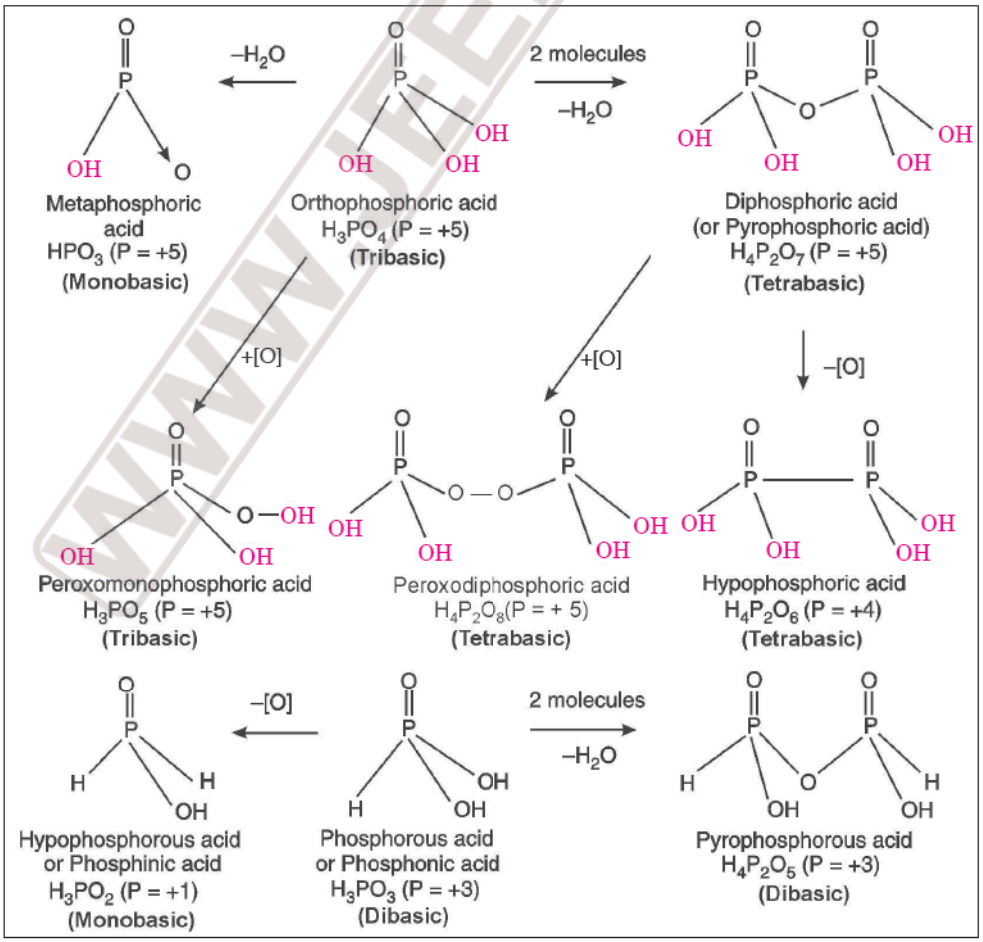
It is used in organic chemistry to reduce arene diazonium salts to arenes.

$$\underset{\substack{\text{Benzene}\\\text{diazonium}\\\text{chloride}}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{C_6H_6} + H_3PO_3 + N_2 + HCl$$

REMEMBER

Peroxomonophosphoric acid (H_3PO_5) and peroxodiphosphoric acid ($H_4P_2O_8$) contain –O–O– linkages.

The structures of different oxoacids of phosphorus are given below :



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The formulae of oxyacids of P can be **remembered** as :
The prefix
- *meta acid* is used for the acid obtained by the loss of one water molecule.
- *pyroacid* is used for the acid obtained by heating two molecules with loss of one water molecule.
- '*hypo*' is generally used for the acid having lower oxygen content than the parent acid.

The main oxoacids of phosphorus acid are summed up below :

SUM UP

Oxoacid	Formula	Characteristic bonds	Method of preparation
Hypophosphorous or Phosphinic	H_3PO_2	One P—OH Two P—H One P=O	$P_4 + 4OH^- + 4H_2O \xrightarrow[NaOH/Ca(OH)_2]{Warm} 4H_2PO_2^- + 2H_2$
Orthophosphorus or Phosphonic	H_3PO_3	Two P—OH One P—H One P=O	$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$ $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$
Pyrophosphorus	$H_4P_2O_5$	Two P—OH Two P—H Two P=O One P—O—P	$PCl_3 + 2H_3PO_3 \longrightarrow H_4P_2O_5 + POCl_3$
Hypophosphoric	$H_4P_2O_6$	Four P—OH Two P=O One P—P	$2P + 2NaClO_2 + 8H_2O \longrightarrow Na_2H_2P_2O_6.6H_2O + 2HCl$ Sod. salt of hypophosphoric acid
Orthophosphoric	H_3PO_4	Three P—OH One P=O	$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$ $P_4 + 20HNO_3 \xrightarrow{Heat} 4H_3PO_4 + 20NO_2 + 4H_2O$ $PCl_5 + 4H_2O \xrightarrow{Heat} H_3PO_4 + 5HCl$
Pyrophosphoric	$H_4P_2O_7$	Four P—OH Two P=O One P—O—P	$2H_3PO_4 \xrightarrow{525\ K} H_4P_2O_7 + H_2O$
Metaphosphoric	HPO_3	Three P—OH Three P=O Three P—O—P for $(HPO_3)_3$	$H_3PO_4 \xrightarrow{525\ K} HPO_3 + H_2O$

SOLVED EXAMPLES

Example 15.

In what way it can be proved that PH_3 is basic in nature. **N.C.E.R.T.**

Solution : PH_3 reacts with acids like HI to form phosphonium iodide, PH_4I.

$$PH_3 + HI \rightarrow \underset{\text{Phosphonium iodide}}{PH_4I}$$

This shows that PH_3 is basic in nature. This basic nature of PH_3 is due to the presence of lone pair on phosphorus atom and therefore, it acts as a Lewis base.

Example 16.

Write the disproportionation reaction of H_3PO_3. (*Assam S.B. 2013*)

Solution : On heating H_3PO_3 disproportionates to give phosphoric acid and phosphine.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

Example 17.

Write balanced equations for the following reactions :

(*a*) $P_4 + NaOH + H_2O \longrightarrow$ (*D.S.B. 2009, Tripura S.B. 2016, Assam S.B. 2016*) (*Assam S.B. 2013*)

(*b*) $As_4 + Cl_2(excess) \longrightarrow$

(*c*) $P_4O_{10} + H_2O \longrightarrow$

(*d*) $Ca_3P_2 + H_2O \longrightarrow$ (*D.S.B. 2008, 2014*)

(*e*) $POCl_3 + H_2O \longrightarrow$

(*f*) $HgCl_2 + PH_3 \longrightarrow$ (*A.I.S.B. 2010*)

(*g*) $Ag + PCl_5 \longrightarrow$ (*A.I.S.B. 2014*)

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Solution :

(*a*) $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$

(*b*) $As_4 + 10Cl_2 \longrightarrow 4AsCl_5$

(*c*) $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

(*d*) $Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$

(*e*) $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$

(*f*) $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$

(*g*) $2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$

❑ Example 18.

Why does PCl_3 fume in moisture ?

N.C.E.R.T. *(Hr.S.B. 2015, 2017, Kerala S.B. 2016)*

Solution : PCl_3 gets hydrolysed in the presence of moisture and gives fumes of HCl.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

❑ Example 19.

Calculate the volume of 0.1 M NaOH solution required to neutralize the solution produced by dissolving 1.1 g of P_4O_6 in water.

Solution : P_4O_6 reacts with water to form phosphorous acid (H_3PO_3) as :

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3 \quad ...(i)$$

H_3PO_3 is dibasic and it neutralizes with NaOH as :

$$H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_3 + 2H_2O \quad ...(ii)$$

Multiply eqn. (*ii*) by 4 and add to eqn. (*i*) :

$$\underset{}{P_4O_6} + \underset{4\times31+6\times16 \atop = 220\ g}{8NaOH} \longrightarrow \underset{8(23+16+1) \atop = 320\ g}{4Na_2HPO_3} + 2H_2O$$

Now 220 g of P_4O_6 require NaOH = 320 g

1.1 g of P_4O_6 will require NaOH for neutralization

$$= \frac{320}{220} \times 1.1 = 1.6\ g$$

Wt. of NaOH present in 1000 mL of 0.1 M NaOH = 4 g

$\therefore$ 4g of 0.1 M NaOH is present in = 1000 mL

$\therefore$ 1.6 g of 0.1 M NaOH is present in

$$= \frac{1000 \times 1.6}{4} = \mathbf{400\ mL}$$

Vol. of 0.1 M NaOH required = **400 mL.**

❑ Example 20.

All the five bonds in PCl_5 are not equivalent. Justify.

N.C.E.R.T. *(A.I.S.B. 2008, D.S.B. 2012, Pb.S.B. 2013, 2015, 2017)*

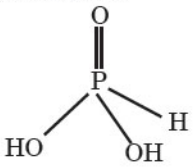
Solution : PCl_5 has trigonal bipyramidal structure in which there are three P—Cl equatorial bonds and two P—Cl axial bonds. The two axial bonds are being repelled by three bond pairs at 90° while the three equatorial bonds are being repelled by two bond pairs at 90°. Therefore, axial bonds are repelled more by bond pairs than equatorial bonds and hence are larger (219 pm) than equatorial bonds (204 pm).

❑ Example 21.

H_3PO_3 is diprotic acid. Explain.

(Hr.S.B. 2005, H.P.S.B. 2015, Pb.S.B. 2013, 2017)

Solution : H_3PO_3 has three H atoms and therefore, it is expected to be tribasic. However, in its structure, two hydrogen atoms are joined through oxygen atoms and are ionisable. The third H atom is linked to P and is non-ionisable.



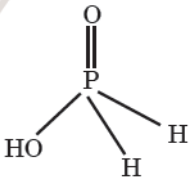
$$H_3PO_3 \rightleftharpoons HPO_3^{2-} + 2H^+$$

❑ Example 22.

How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure.

N.C.E.R.T. *(Assam S.B. 2016)*

Solution : H_3PO_2 has one P═O, one P—OH and two P—H bonds as.



Since two H atoms are bonded directly to P atom which impart reducing character to the acid.

❑ Example 23.

What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2 ?

N.C.E.R.T.

Solution : Phosphine is formed.

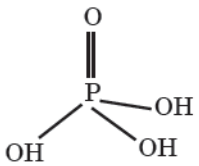
$$P_4 + 3NaOH + 3H_2O \xrightarrow{\text{Heat}} \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

❑ Example 24.

What is the basicity of H_3PO_4?

N.C.E.R.T. *(A.I.S.B. 2014, H.P.S.B. 2017)*

Solution : H_3PO_4 contains three P–OH bonds and therefore, its basicity is three.



❑ Example 25.

What happens when

(i) $(NH_4)_2Cr_2O_7$ is heated?

(ii) PCl_5 is heated? *(H.P.S.B. 2015)*

(iii) H_3PO_3 is heated? Write the equations involved.

(A.I.S.B. 2015, D.S.B. 2008, 2013, 2017)

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Solution :

(*i*) On heating $(NH_4)_2Cr_2O_7$, nitrogen gas is evolved.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} Cr_2O_3 + N_2 + 4H_2O$$

(*ii*) On heating, PCl_5 first sublimes and then decomposes on strong heating :

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

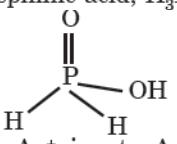
(*iii*) On heating, H_3PO_3 disproportionates to give orthophosphoric acid and phosphine.

$$\overset{+3}{4H_3PO_3} \longrightarrow \underset{\text{Orthophosphoric acid}}{\overset{+5}{3H_3PO_4}} + \underset{\text{Phosphine}}{\overset{-3}{PH_3}}$$

Example 26.

(i) Draw the structure of phosphinic acid (H_3PO_2).
(ii) Write a chemical reaction for its use as reducing agent. *(C.B.S.E. Sample Paper 2011)*

Solution : (*i*) Phosphinic acid, H_3PO_2.



(*ii*) H_3PO_2 reduces Ag^+ ion to Ag which shows its reducing nature.

$$H_3PO_2 + 4AgNO_3 + 2H_2O \longrightarrow 4Ag + 4HNO_3 + H_3PO_4$$

Example 27.

(a) Suggest a quantitative method for estimation of the gas which protects us from U.V. rays of the sun.
(b) Nitrogen oxides emitted from the exhaust system of supersonic jet aeroplanes slowly deplete the concentration of ozone layer in upper atmosphere. Comment. *(C.B.S.E. Sample Paper 2011)*

Solution : (*a*) The gas which protects us from U.V. rays of the sun is ozone. It reacts with I^- ions to give iodine as :

$$O_3 + 2I^- + H_2O \longrightarrow O_2 + I_2 + 2OH^-$$

I_2 liberated is titrated against sodium thiosulphate solution and amount of O_3 can be estimated.

(*b*) The release of nitrogen oxides (NO_x) into stratosphere by the exhaust system of supersonic jet aeroplanes deplete the concentration of O_3 because NO reacts with O_3 to give O_2.

$$NO\ (g) + O_3\ (g) \longrightarrow NO_2\ (g) + O_2\ (g)$$

Therefore, NO is slowly depleting the concentration of ozone.

Example 28.

NCl_3 is readily hydrolysed while NF_3 does not. Explain.

Solution : In NCl_3, Cl has vacant *d*-orbitals to accept the lone pair of electrons donated by oxygen atom of H_2O molecules. But in NF_3, F does not have vacant *d*-orbitals. Therefore, NCl_3 undergoes hydrolysis but NF_3 does not.

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$$
$$NF_3 + H_2O \longrightarrow \text{No reaction}$$

Example 29.

Among the hydrides of Group 15 elements, which have the
(a) lowest boiling point?
(b) maximum basic character?
(c) highest bond angle?
(d) maximum reducing character? *(A.I.S.B. 2018)*

Solution : (*a*) PH_3 (*b*) NH_3
(*c*) NH_3 (*d*) BiH_3

Practice Problems

13. Give one example each of oxyacid of P having the oxidation state
(*i*) +4 (*ii*) +3

14. What is the chemical formula of laughing gas ? How is it prepared ?

15. Among the hydrides of group 15, predict the hydride having
(*i*) most basic character
(*ii*) highest thermal stability
(*iii*) lowest boiling point
(*iv*) strongest reducing agent.

16. Name the oxide of nitrogen obtained in the following reactions :
(*i*) $Pb(NO_3)_2 \xrightarrow[673\ K]{\text{Heat}}$
(*ii*) $NH_4NO_3 \xrightarrow{\text{Heat}}$
(*iii*) $N_2O_4 + NO \xrightarrow{250\ K}$

17. What is the oxidation state of phosphorus in the following :
(*i*) H_3PO_3 (*ii*) PCl_3
(*iii*) Ca_3P_2 (*iv*) Na_3PO_4
(*v*) POF_3

18. Which of the following has maximum P—OH bonds ?
(*i*) Orthophosphoric acid
(*ii*) Pyrophorous acid
(*iii*) Pyrophosphoric acid

19. Name the oxoacid of P which
(*i*) exists as polymeric
(*ii*) has basicity two

20. Name three oxoacids of P having oxidation state of P as +5.

Answers to Practice Problems

13. (*i*) Hypophosphoric (*ii*) Phosphorus acid
14. N_2O.
15. (*i*) NH_3 (*ii*) NH_3 (*iii*) PH_3 (*iv*) BiH_3.
16. (*i*) Nitrogen dioxide
(*ii*) Nitrous oxide
(*iii*) Dinitrogen trioxide.
17. (*i*) +3 (*ii*) +3 (*iii*) –3 (*iv*) +5 (*v*) +5.
18. (*iii*)
19. (*i*) Metaphosphoric acid
(*ii*) Phosphonic acid
20. orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid

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add on

Conceptual Questions

CONCEPTUAL QA

Q.1. Draw the structure of P_4O_{10} and identify the number of single and double P–O bonds.

Ans. *See text.* Double bonds = 4, single bonds = 12.

Q.2. Nitric oxide becomes brown when released in air.

Ans. When nitric oxide, NO is released in air, it becomes brown due to the formation of NO_2 (nitrogen dioxide), which is a brown gas.

$$2NO\,(g) + O_2\,(g) \longrightarrow \underset{\text{(Brown)}}{2NO_2\,(g)}$$

Q.3. Solid PCl_5 is ionic in nature. ***(A.I.S.B. 2016)***

Ans. PCl_5 is ionic in the solid state because it exists as $[PCl_4]^+\,[PCl_6]^-$ in which the cation is tetrahedral and anion is octahedral.

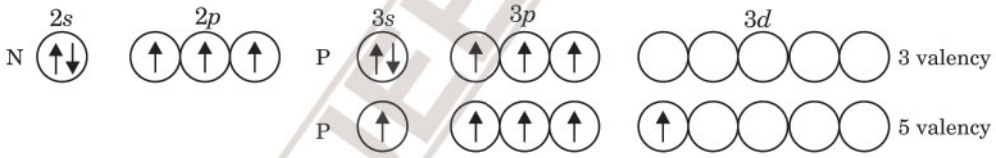
Q.4. Concentrated nitric acid turns yellow on exposure to sunlight. Why ?

Ans. On exposure to sunlight, nitric acid decomposes into NO_2, O_2 and H_2O. The presence of NO_2 in the partially decomposed nitric acid gives it yellow colour.

$$4HNO_3\,(l) \longrightarrow 4NO_2(g) + O_2\,(g) + 2H_2O\,(l)$$

Q.5. Why does not nitrogen form pentahalides like phosphorus ?

Ans. Nitrogen does not have vacant *d*-orbitals in its valence shell. Therefore, it cannot extend its valency beyond 3. Therefore, it can form maximum of four bonds and cannot form pentahalides. On the other hand, phosphorus has vacant 3*d*-orbitals in the valence shell and therefore, one electron can be easily promoted from valence 3*s*-orbital to vacant 3*d*-orbital. Thus, it can exhibit pentavalency in its compounds.



Q.6. Determine the oxidation number of nitrogen in *(i)* N_2O *(ii)* NO_2 *(iii)* HNO_3 *(iv)* NH_3.

Ans. *(i)* N_2O : + 1 *(ii)* NO_2 : + 4 *(iii)* HNO_3 : + 5 *(iv)* NH_3: – 3

Q.7. How is pyrophosphoric acid related to orthophosphoric acid?

Ans. Pyrophosphoric acid ($H_4P_2O_7$) is the anhydride of orthophosphoric acid (H_3PO_4) and is obtained by the removal of a molecule of water from two molecules of H_3PO_4 as shown below:

$$\underset{\text{Orthophosphoric acid}}{2H_3PO_4} \xrightarrow{527\ K} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} + H_2O$$

Q.8. N_2O supports combustion more vigorously than air. Explain.

Ans. N_2O decomposes to give O_2 which is about 1/3 of the volume of gases produced ($2N_2 + O_2$).

$$2N_2O \xrightarrow{\text{Heat}} 2N_2 + O_2$$

On the other hand, air contains 1/5th part of O_2 of its volume. Due to larger content of O_2, N_2O supports combustion more vigorously than air.

Q.9. On being slowly passed through water, PH_3 forms bubbles but NH_3 dissolves. Why?

Ans. N—H bond in ammonia is more polar than P—H bond in phosphine. Therefore, NH_3 forms hydrogen bonds with water molecules and hence dissolves in it. On the other hand, PH_3 does not dissolve and hence forms bubbles.

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CONCEPTUAL QA

Q.10. Write the reaction of thermal decomposition of sodium azide.

Ans. Thermal decomposition of sodium azide gives nitrogen gas.

$$2NaN_3 \longrightarrow 2Na + 3N_2$$

Sodium azide

Q.11. Phosphoric acid has high viscosity and high melting point. Why ?

Ans. Phosphoric acid has a tendency to form hydrogen bonding in concentrated solutions. Therefore, it has high viscosity and is a syrupy liquid and has high boiling point.

Q.12. PCl_5 exists as $[PCl_6]^-$ $[PCl_4]^+$ but PBr_5 exists as $[PBr_4]^+$ $[Br]^-$. Explain.

Ans. Both PCl_5 and PBr_5 have trigonal bipyramidal geometry. This is not a regular structure and is not very stable. Therefore, PCl_5 splits up into more stable octahedral and tetrahedral structures, which are stable than trigonal bipyramidal.

$$PCl_5 \rightleftharpoons [PCl_6]^- [PCl_4]^+$$

On the other hand, PBr_5 splits up into stable tetrahedral structure as

$$[PBr_5] \rightleftharpoons [PBr_4]^+ [Br]^-$$

This splitting is different from PCl_5 because Br atoms are large and six atoms of Br cannot be easily accommodated around smaller P atom.

Q.13. PCl_5 is known but PI_5 is not known. Why ?

Ans. Due to small size of Cl atom, five Cl atoms can be accommodated around P atom. But I is of large size and therefore, five I atoms cannot be accommodated around P atom. As a result, P–I bonds are weak and prefer to form PI_3 rather than PI_5. Therefore, PI_5 is unstable.

Q.14. Write the structural difference between white P and red P. ***(D.S.B. 2014)***

Ans. White P consists of P_4 units in which four P atoms lie at the corners of a regular tetrahedron with $\angle PPP = 60°$.

Red P also consists of P_4 tetrahedra units but it has polymeric structure consisting of P_4 tetrahedra linked together by covalent bonds.

Q.15. What is liquid nitrogen used for ?

Ans. Liquid nitrogen is used as a refrigerant to preserve biological specimens. It is also used to provide low temperature.

Q.16. Why does iron become passive when dipped in conc. HNO_3 ?

Ans. Iron becomes passive when dipped in conc. HNO_3 due to the formation of a thin protective layer of the metal oxide on its surface. This protective layer corresponds to ferrosoferric oxide, $FeO.Fe_2O_3$ and prevents further action of the metal.

Q.17. What is calcium cyanamide ? Why is it used as a fertilizer ?

Ans. Calcium cyanamide is $CaCN_2$. It reacts with water to form ammonia.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

So, it can provide nitrogen nutrient to the soil and plants. Therefore, it is used as a fertilizer under the name **nitrolim** ($CaCN_2 + C$).

Q.18. In the ring test of nitrates, what chemical compound is formed ?

Ans. $[Fe(H_2O)_5\ NO]SO_4$.

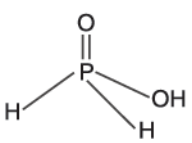
Q.19. What is azote ?

Ans. Azote is the name given to nitrogen by Lavoisier.

Q.20. What is the basicity of H_3PO_2 acid and why ?

(A.I.S.B. 2012)

Ans. H_3PO_2 has the structure :



It has only one ionisable hydrogen and therefore, its basicity is one.

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Q.21. Write down the balanced chemical equation representing action of HNO_3 on sulphur and iodine.

Ans. (*i*) Action of HNO_3 on S

$$\frac{1}{8}S_8(s) + 6HNO_3 \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_4} + 6NO_2 + 2H_2O$$

(*ii*) Action of HNO_3 on I

$$I_2(s) + 10HNO_3 \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10NO_2 + 4H_2O$$

Q.22. Give examples of oxide of nitrogen

(*a*) blue liquid below 253 K **(*b*) known as laughing gas**

(*c*) brown gas **(*d*) colourless gas having oxidation state of N equal to 5**

(*e*) prepared by heating lead nitrate.

Ans. (*a*) N_2O_3 (*b*) N_2O (*c*) NO_2 (*d*) N_2O_5 (*e*) NO_2.

Q.23. How would you prepare a sample of deuterated ammonia, ND_3 ?

Ans. It is prepared by the action of heavy water on magnesium nitride.

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + \underset{\text{Deuterated ammonia}}{2ND_3}$$

Q.24. N_2O supports combustion more vigorously than air. Explain.

Ans. N_2O decomposes to give O_2 which is about 1/3 of the volume of gases produced ($2N_2 + O_2$).

$$2N_2O \xrightarrow{\text{Heat}} 2N_2 + O_2$$

On the other hand, air contains 1/5th part of O_2 of its volume. Due to larger content of O_2, N_2O supports combustion more vigorously than air.

Q.25. Name the promoter used in Haber's process. ***(C.B.S.E. Sample Paper 2017-18)***

Ans. Molybdenum.

Q.26. Which one of PCl_4^+ and PCl_4^- is not likely to exist and why ? ***(D.S.B. 2012)***

Ans. PCl_4^- is not likely to exist because lone pair on P in PCl_3 can be donated to Cl^+ and not to Cl^-.

Q.27. Which is a stronger reducing agent, SbH_3 or BiH_3 and why ? ***(A.I.S.B. 2012)***

Ans. BiH_3 is a stronger reducing agent than SbH_3. This is because BiH_3 is less stable than SbH_3 because of larger size of Bi than Sb.

Q.28. NF_3 is an exothermic compound whereas NCl_3 is not. Explain. ***(A.I.S.B. 2011, 2012)***

Ans. NF_3 is an exothermic compound while NCl_3 is not because :

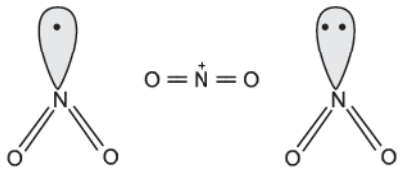
(*i*) The bond dissociation enthalpy of F_2 is lower than that of Cl_2.

(*ii*) Size of F is small as compared to Cl and therefore F forms stronger bonds with nitrogen releasing large amount of energy.

Therefore, overall energy is released during the formation of NF_3 and energy is absorbed during the formation of NCl_3.

Q.29. The bond angles (O—N—O) are not of the same value in NO_2^- and NO_2^+. ***(D.S.B. 2012)***

Ans. In NO_2 there is one electron on N. Therefore, in NO_2^+, there is no electron on N atom and there is a lone pair of electrons on N atom in NO_2^-.



NO_2^+ is linear and has bond angle of 180°. Because of repulsions by a lone air of electrons in NO_2^-, the molecule has angular shape and bond angle has been found to be 115°. Hence, the bond angles in NO_2^+ and NO_2^- are different.

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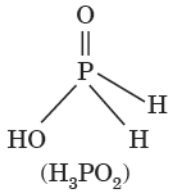
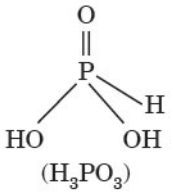
Q.30. H_3PO_2 is a stronger reducing agent than H_3PO_3.

(A.I.S.B. 2014, 2016)

Ans. The reducing character of the acid is due to H atoms bonded directly to P atom. In H_3PO_2, there are two P–H bonds whereas in H_3PO_3, there is one P–H bond. Therefore, H_3PO_2 is a stronger reducing agent than H_3PO_3.



(H_3PO_2)



(H_3PO_3)

Q.31. Bi(V) is a stronger oxidizing agent than Sb(V). ***(D.S.B. 2014)***

Ans. On moving down the group, the stability of +5 oxidation state decreases while the stability of +3 oxidation state increases due to inert pair effect. Therefore, +5 oxidation state of Bi is less stable than +5 oxidation state of Sb. Thus, Bi(V) is a stronger oxidising agent than Sb(V).

Q.32. N—N single bond is weaker than P—P single bond. ***(D.S.B. 2014)***

Ans. N—N single bond is weaker than P—P single bond because of high interelectronic repulsions of non-bonding electrons due to small bond length.

Q.33. What happens when orthophosphorous acid is heated? ***(C.B.S.E Sample Paper 2017-18)***

Ans. Phosphoric acid and phosphine are formed.

$$4H_3PO_3 \xrightarrow[475\ K]{Heat} 3H_3PO_4 + PH_3$$

QUICK CHAPTER ROUND UP

GROUP 15 ELEMENTS

- **General electronic configuration:** ns^2np^3
- N, P, As, Sb, Bi
- Nitrogen differs from other elements of the group due to
  - ❑ small size,
  - ❑ high electronegativity,
  - ❑ absence of d – orbitals in the valence shell
  - ❑ tendency to form $p\pi$–$p\pi$ bonds with itself and with highly electronegative atoms (O or C).
- Elements of group 15 exhibit two oxidation states +3 and +5 but +3 oxidation state is formed because of inert pair effect.
  Nitrogen does not form compounds in +5 oxidation state such as NCl_5 and NF_5, etc, because of the absence of d-orbitals in its valence shell.
- In hydrides :
  Bond angle : $NH_3 > PH_3 > AsH_3 > SbH_3$
  Basic character : $NH_3 > PH_3 > AsH_3$
  Boiling point : $NH_3 > PH_3 < AsH_3 < SbH_3$
  Stability : $NH_3 > PH_3 > AsH_3 > SbH_3$
  Reducing character : $NH_3 < PH_3 < AsH_3$.
- NH_3 is manufactured by Haber's process.
- N also forms hydrides such as hydrazine (N_2H_4) and hydrazoic acid (HN_3).
- N_2O (colourless, neutral), NO (colourless, neutral), N_2O_3 (pale blue solid, acidic), N_2O_4 (colourless solid, acidic), NO_2 (Brown gas, acidic), N_2O_5 (colourless solid or gas, acidic)
- N_2O is called laughing gas and is obtained by heating NH_4NO_3.
- Phosphorus exists as P_4 in elemental state and exists in several allotropic forms.
- Black P is most stable and least reactive allotropic form of P. White P is least stable and most reactive. Black P has polymeric structure.

$$P_4 + 3O_2 \text{ (limited)} \longrightarrow P_4O_6$$
$$P_4 + 5O_2 \text{ (excess)} \longrightarrow P_4O_{10}$$
$$P_4O_6 + 6H_2O \text{ (cold)} \longrightarrow 4H_3PO_3$$
$$P_4O_6 + 6H_2O \text{ (hot)} \longrightarrow 3H_3PO_4 + PH_3$$
$$P_4O_{10} + 2H_2O \text{ (cold)} \longrightarrow 4H_3PO_3$$
$$P_4O_{10} + 6H_2O \text{ (hot)} \longrightarrow 4H_3PO_4$$

Phosphorus forms a number of oxoacids. Depending upon the number of P—OH bonds, they have different basicity.
Hypophosphorous acid, H_3PO_2 (Basicity = 1),
Phosphonic acid, H_3PO_3 (Basicity = 2),
Orthophosphoric acid, H_3PO_4 (Basicity = 3),
Pyrophosphoric acid, $H_4P_2O_7$ (Basicity = 4).

- The oxoacids having P—H bonds are good reducing agents.
- In solid state PCl_5 exists as $[PCl_4]^+[PCl_6]^-$.

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NCERT FILE Solved

NCERT In-text Questions

Q.1. Why are pentahalides more covalent than trihalides?

Ans. In pentahalides, the oxidation state is more (+5) than in trihalides (+3). As a result of higher positive oxidation state of central atom, they have larger polarizing power and can polarise the halide ion(X^-) to a greater extent than in the corresponding trihalide. Since larger the polarisation, larger is the covalent character, therefore, pentahalides are more convalent than trihalides.

Q.2. Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15?

Ans. Among the hydrides of group 15, BiH_3 is least stable because Bi has largest size in the group and has least tendency to form covalent bond with small hydrogen atom. Therefore, it can readily lost H atom and has strongest tendency to act as reducing agent.

Q.3. Why is N_2 less reactive at room temperature?

Ans. *Refer Solved Example 3 (Page 10)*

Q.4. Mention the conditions required to maximise the yield of ammonia.

Ans. Ammonia is formed according to the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H° = -46.1 kJ\ mol^{-1}$$

The conditions for maximum yield of ammonia are:

(*i*) Low temperature of the order of about 700 K

(*ii*) High pressure of 200×10^5 Pa (about 200 atm).

(*iii*) Presence of catalyst such as iron oxide with small amount of K_2O and Al_2O_3

Q.5. How does ammonia react with a solution of Cu^{2+}?

Ans. Ammonia reacts with a solution of Cu^{2+} to form deep blue coloured complex, tetraamminecopper (II) ion:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

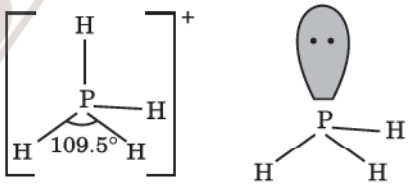
Tetraamminecopper (II) ion (deep blue)

Q.6. What is the covalence of nitrogen in N_2O_5?

Ans. *Refer Solved Example 14 (Page 23).*

Q.7. Bond angle in PH_4^+ is higher than that in PH_3. Why?

Ans. Both PH_4^+ and PH_3 involve sp^3 hybridisation of P atom. In PH_4^+ all the four orbitals are bonded, whereas in PH_3 there is a lone pair of electrons on P. In PH_4^+, the HPH bond angle is tetrahedral angle of 109.5°. But in PH_3, lone pair-bond pair repulsion is more than bond pair-bond pair repulsion so that bond angles become less than normal tetrahedral angle of 109.5°. The bond angle in PH_3 has been found to be about 93.6°.



Q.8. What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2?

Ans. *Refer Solved Example 23 (Page 35).*

Q.9. What happens when PCl_5 is heated?

Ans. *Refer Solved Example 25 (Page 35).*

Q.10. Write a balanced equation for the hydrolytic reaction of PCl_5 with heavy water.

Ans. $PCl_5 + D_2O \longrightarrow POCl_3 + 2DCl$

Q.11. What is the basicity of H_3PO_4?

Ans. *Refer Solved Example 24 (Page 35)*

Q.12. What happens when H_3PO_3 is heated?

Ans. *Refer Solved Example 25 (Page 35)*

NCERT Textbook Exercises

Q.1. Discuss the general characteristics of group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionization enthalpy and electronegativity.

Ans. *Refer Text (Pages 2-4).*

Q.2. Why does the reactivity of nitrogen differ from phosphorus?

Ans. Nitrogen has a unique ability to form $p\pi$–$p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (*e.g.*, C, O). Therefore, it has triple bond between two nitrogen atoms (N ≡ N) and is non-polar. Due to triple bond it has very high bond enthalpy (941.4kJ) and therefore, it does not react with other elements under normal

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conditions and is very unreactive. On the other hand, phosphorus forms single bond (P–P) and is reactive in comparison to nitrogen.

Q.3. Discuss the trends in chemical reactivity of group 15 elements.

Ans. *Refer Text Page 4.*

Q.4. Why does NH_3 forms hydrogen bonds but PH_3 does not?

Ans. Because of high electronegativity and small size of nitrogen, ammonia forms hydrogen bonds. On the other hand, P has low electronegativity and large size and hence cannot form hydrogen bonds.

Q.5. How is nitrogen prepared in the laboratory? Write the chemical equation of the reactions involved.

Ans. In the laboratory, nitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + NaCl(aq) + 2H_2O(l)$$

It may be noted that small amounts of NO and HNO_3 are also formed in this reaction as impurities. These are removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

Q.6. How is ammonia manufactured industrially?

Ans. Ammonia is manufactured industrially by Haber's process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$\Delta_f H^\circ = -46.1$ kJ mol^{-1}

The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), at temperature of about 700 K and a catalyst iron oxide with small amounts of K_2O and Al_2O_3.

For detail refer Text (Page 13).

Q.7. Illustrate how copper metal can give different products on reaction with HNO_3.

Ans. Concentrated nitric acid is a strong oxidising agent and reacts with metals. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation. For example, copper reacts with HNO_3 giving different products as:

Conc. HNO_3 gives copper nitrate and nitrogen dioxide.

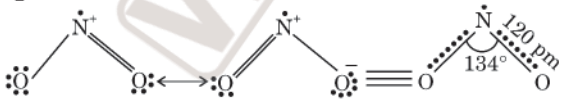
$$Cu + \underset{\text{conc.}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Dilute HNO_3 gives copper nitrate and nitric oxide.

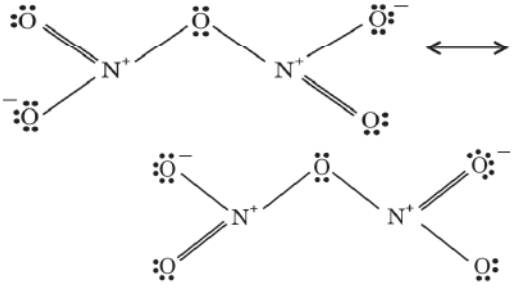
$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Q.8. Give the resonating structures of NO_2 and N_2O_5.

NO_2

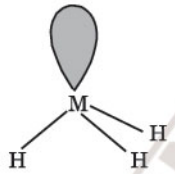


N_2O_5



Q.9. The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?

Ans. All the hydrides of group (NH_3, PH_3, AsH_3 and SbH_3) involve sp^3 hybridisation of the central atom in which one of the position is occupied by a lone pair of electrons.



(M = N, P, As, Sb)

Now, as we move down the group from N to P to As to Sb, the size of the atom goes on increasing and its electronegativity decreases. Consequently, the position of bond pair shifts more and more away from the central atom in moving form NH_3 to SbH_3. For example, the bond pair in NH_3 is close to N in N–H bond than the bond pair in P–H bond in PH_3. As a result, the force of repulsion between the bonded pair of electrons in NH_3 is more than in PH_3. In general, the force of repulsion between bonded pairs of electrons decreases as we move from NH_3 to BiH_3 and therefore, the bond angle also decreases in the same order.

Q.10. Why does $R_3P = O$ exists but $R_3N = O$ does not (R = alkyl group). *(A.I.S.B. 2014)*

Ans. $R_3N = O$ does not exist because nitrogen cannot have covalency more than four. Moreover, $R_3P = O$ exists because phosphorus can extend its covalency more than 4 as well as it can form $d\pi$-$p\pi$ bond whereas nitrogen cannot form $d\pi$-$p\pi$ bond.

Q.11. Explain why NH_3 is basic while BiH_3 is only feebly basic.

Ans. Both N and Bi have a lone pair of electrons in NH_3 and BiH_3 respectively. They can donate the electron pair and therefore behave as Lewis base. In NH_3, N has small size and the lone pair is concentrated on a small region and electron density on it is maximum. Consequently, it has greater electron releasing tendency. But the size of Bi is large and the electron density of the lone pair is less. As a result, it has lesser tendency to donate electron pair. Hence, NH_3 is basic while BiH_3 is only feebly basic.

Q.12. Nitrogen exists as diatomic molecule and phosphorus as P_4. Why ?

Ans. *Refer Solved Example 1 (Page 10)*

Q.13. Write main differences between the properties of white phosphorus and red phosphorus.

Ans. The main differences between white phosphorus and red phosphorus are:

Properties	White phosphorus	Red phosphorus
Colour	White but turns yellow on exposure	Dark red
State	Waxy solid	Brittle powder
Density	1.84 g cm^{-3}	2.1 g cm^{-3}
Ignition temperature	307 K	543 K
Stability	Less stable at ordinary temperature	More stable at ordinary temperature
Chemical reactivity	Very reactive	Less reactive

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Q.14. Why does nitrogen shows catenation properties less than phosphorus?

Ans. *Refer Solved Example 5 (Page 11).*

Q.15. Give the disproportionation reaction of H_3PO_3.

Ans. H_3PO_3 disproportionate on heating as :

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

Q.16. Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

Ans. Phosphorus can show maximum oxidation state of +5 in its compounds. In PCl_5, its oxidation state is +5. Since it cannot increase its oxidation state beyond +5, it cannot act as a reducing agent. However, it can act as an oxidising agent by undergoing decrease in its oxidation state from +5 to +3. For example, it oxidises silver to AgCl, Sn to $SnCl_4$ etc.

$$\overset{0}{2Ag} + \overset{+5}{PCl_5} \longrightarrow \overset{+1}{2AgCl} + \overset{+3}{PCl_3}$$

NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 56A.*

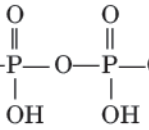
Short Answer Type Questions

1. Write a balanced chemical equation for the reaction showing catalytic oxidation of NH_3 by atmospheric oxygen.

Ans. $4NH_3 + 5O_2 \xrightarrow[500\ K,\ 9\ bar]{Pt/Rh\ gauge\ catalyst} 4NO + 6H_2O$

2. Write the structure of pyrophosphoric acid.

Ans.



Pyrophosphoric acid

3. PH_3 forms bubbles when passed slowly in water but NH_3 dissolves. Explain why?

Ans. NH_3 forms hydrogen bonds with water and therefore soluble in water but PH_3 cannot form hydrogen bonds with water and therefore, is not soluble in water. It escapes as gas.

4. In PCl_5, phosphorus is in sp^3d hybridised state but all its five bonds are not equivalent. Justify your answer with reason.

Ans. It has trigonal bipyramidal geometry in which all the four bonds are not equal.

5. Why is nitric oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic?

Ans. In gaseous state NO_2 exists as monomer which has one unpaired electron. In the solid state it dimerises to N_2O_4 so no unpaired electron is left hence solid form is diamagnetic.

6. In the ring test of NO_3^- ion, Fe^{2+} ion reduces nitrate ion to nitric oxide, which combines with Fe^{2+} (aq) ion to form brown complex. Write the reactions involved in the formation of brown ring.

Ans. $NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$

$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$

(brown complex)

7. P_4O_6 reacts with water according to equation:

$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

Calculate the volume of 0.1 M NaOH solution required to neutralise the acid formed by dissolving 1.1 g of P_4O_6 in H_2O.

Ans. $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$

H_3PO_3 can be neutralised with NaOH as :

$4H_3PO_3 + 8NaOH \longrightarrow 4Na_2HPO_3 + 8H_2O$

$$\underset{1\ mol}{P_4O_6} + \underset{8\ mol}{8NaOH} \longrightarrow 4Na_2HPO_3 + 2H_2O$$

Moles of $P_4O_6 = \frac{1.1}{220} = 0.005$ mol

Acid formed by 1 mol of P_4O_6 require NaOH = 8 mol

Acid formed by 0.005 mol of P_4O_6 require NaOH = $8 \times 0.005 = 0.04$ mol

0.1 M NaOH means 0.1 mol of NaOH is present in 1000 mL solution

0.04 M of NaOH is present in solution = $\frac{1000}{0.1} \times 0.04$

= 400 mL

8. White phosphorus reacts with chlorine and the product hydrolyses in the presence of water. Calculate the mass of HCl obtained by the hydrolysis of the product formed by the reaction of 62 g of white phosphorus with chlorine in the presence of water.

Ans. Phosphorus react with Cl_2 as :

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$

PCl_3 is hydrolysed as :

$PCl_3 + 3H_2O \longrightarrow 3H_3PO_3 + 3HCl\ ] \times 4$

$P_4 + 6Cl_2 + 12H_2O \longrightarrow 4H_3PO_3 + 12HCl$

Moles of white P = $\frac{62}{124} = 0.5$ mol

1 mol of white P_4 produces HCl = 12 mol

0.5 mol of white P_4 will produce HCl = $12 \times 0.5 = 6$ mol

Mass of HCl = $6 \times 36.5 = 219.0$ g

9. Name three oxoacids of nitrogen. Write the disproportionation reaction of that oxoacid of nitrogen in which nitrogen is in +3 oxidation state.

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Ans. Three oxoacids of nitrogen are
(*i*) HNO_2, Nitrous acid (*ii*) HNO_3, Nitric acid
(*iii*) Hyponitrous acid, $H_2N_2O_2$
Acid in which oxidation state of N is + 3, is HNO_2

$$3HNO_2 \xrightarrow{\text{Disproportionation}} HNO_3 + H_2O + 2NO$$

10. Nitric acid forms an oxide of nitrogen on reaction with P_4O_{10}. Write the reaction involved. Also write the resonating structures of the oxide of nitrogen formed.

Ans. Reaction of nitric acid and P_4O_{10}.

$$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$$

Resonating structures of N_2O_5 :

11. Phosphorus has three allotropic forms — (*i*) white phosphorus (*ii*) red phosphorus and (*iii*) black phosphorus. Write the difference between white and red phosphorus on the basis of their structure and reactivity.

Ans. For structures of three allotropes of P, refer chapter in Brief.

Differences between white P and red P

White phosphorus has discrete P_4 units. The four P atoms lie at the corners of a regular tetrahedron with ∠PPP = 60°. Each P is bonded to each of the other three P atoms by covalent bonds so that each P completes its valence shell.

Red phosphorus also consists of P_4 units but have polymeric structure consisting of P_4 tetrahedra linked together through P—P bonds to form the chain.

Reactivity. White phosphorus is much more reactive than red phosphorus. This is because in white phosphorus, there is angular strain in P_4 molecules because the bond angles are only 60°.

12. Give an example to show the effect of concentration of nitric acid on the formation of oxidation product.

Ans. Dilute and concentrated nitric acid give different oxidation products on reaction with metals. For example, copper reacts with dilute and conc. HNO_3 as:

$$3Cu + 8HNO_3 \text{ (dil.)} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3 \text{ (Conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

13. PCl_5 reacts with finely divided silver on heating and a white silver salt is obtained, which dissolves on adding excess aqueous NH_3 solution. Write the reactions involved to explain what happens.

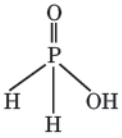
Ans. PCl_5 reacts with silver to form white silver salt (AgCl). This dissolves in aqueous ammonia to form soluble complex.

$$PCl_5 + 2Ag \longrightarrow \underset{\text{White ppt}}{2AgCl} + PCl_3$$

$$AgCl + 2NH_3\,(aq) \longrightarrow \underset{\text{Soluble complex}}{[Ag(NH_3)_2]^+ Cl^-}$$

14. Phosphorus forms a number of oxoacids. Out of these oxoacids phosphinic acid has strong reducing property. Write its structure and also write a reaction showing its reducing behaviour.

Ans. Structure of phosphinic acid (Hypophosphorous acid) is as follows:



Reducing behaviour of phosphinic acid is observed when it reacts with silver nitrate as:

$$4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3 + H_3PO_4.$$

QUICK MEMORY TEST

A. Say True or False

1. The covalence of N_2O_5 is five.
2. H_3PO_2 is a dibasic acid.
3. All the five bonds in PCl_5 are not equal.
4. NH_3 is less basic than PH_3.
5. Both pyrophosphoric acid and hypophosphoric acid have P–O–P linkages.
6. White phosphorous is most reactive while black phosphorus is least reactive.
7. Nitrogen cannot form compounds of the type R_3N = O while phosphorus can form compounds of the type R_3P=O.
8. As_2O_5 is amphoteric while Sb_2O_5 is acidic.
9. Phosphine is poisonous while ammonia is non-poisonous.
10. Oxidation state of N in peroxonitric acid is +7.

B. Complete the missing links

1. Calcium phosphide on hydrolysis gives ..... and calcium hydroxide.
2. Concentrated nitric acid on dehydration with P_4O_{10} gives .....
3. The formula of acidic nitrogen hydride is .....
4. In brown ring test for nitrates, Fe^{2+} ion reduces NO_3^- ion to ..... which reacts with Fe^{2+} ion to form a

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brown ring complex having the molecular formula .....

5. PCl_5 in solid state exists as ionic compound having cation ..... and anion .....
6. Nitrogen is a gas because of its tendency to form .....
7. The two neutral oxides of nitrogen are ..... and .....
8. In gaseous state nitric oxide is ..... while in the liquid or solid state it is .....
9. Among group 15 hydrides, ... is most stable.
10. P_4O_6 and P_4O_{10} dissolve in water to give ..... and .....
11. Calcium cyanamide is used as fertilizer under the name .....
12. The oxide of nitrogen obtained on heating lead nitrate is .....
13. Phosphorus reacts with nitric acid to form ..... acid.
14. Laughing gas is obtained on heating a mixture of NH_4Cl and ..... but nitrogen gas is obtained when a mixture of NH_4Cl and ..... is heated.
15. Hypophosphoric acid is ..... basic but pyrophosphorous acid is ..... basic.
16. Orthophosphorous acid on heating gives ..... and .....

C. Choose the correct alternative

1. Nitrogen gas is obtained by heating *ammonium nitrite / ammonium nitrate.*
2. White phosphorus is *less / more* reactive than red phosphorus.
3. N_2O is obtained by heating NH_4NO_3 / NH_4NO_2.
4. The polymeric allotrope of phosphorus is black/white phosphorus.
5. P_4O_6 dissolves in cold water to give H_3PO_3/H_3PO_4.

Answers QUICK MEMORY TEST

A. Say True or False

1. **False.** Maximum covalence of nitrogen cannot be more than 4 because of absence of *d*-orbitals.
2. **False.** H_3PO_2 is monobasic because it has only one ionisable hydrogen atom.
3. True.
4. **False.** NH_3 is more basic than PH_3.
5. **False.** Pyrophosphoric acid has P–O–P linkage but hypophosphoric acid does not have P–O–P linkage. It has only P–P linkage.
6. True **7.** True
8. **False.** Acidic character decreases while basic character increases down the group and therefore, As_2O_5 is acidic while Sb_2O_5 is amphoteric.
9. True **10.** False : Oxidation state of N is +5.

B. Complete the missing links

1. phosphine
2. N_2O_5 **3.** N_3H
4. NO, $[Fe(H_2O)_5NO]^{2+}$ **5.** $PCl_4^+PCl_6^-$
6. multiple bonds
7. N_2O, NO **8.** paramagnetic, diamagnetic
9. NH_3 **10.** H_3PO_3, H_3PO_4 **11.** nitrolim
12. NO_2 **13.** phosphoric
14. $NaNO_3$, $NaNO_2$ **15.** tetra, di
16. phosphoric acid, phosphine

C. Choose the correct alternative

1. ammonium nitrite **2.** more. **3.** NH_4NO_3
4. black **5.** H_3PO_3

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Elemental phosphorus does not exist as P_2 like N_2. Why ?

Ans. Nitrogen has a strong tendency to form multiple bonds because of its small size and high electronegativity. Therefore, it exists as a diatomic molecule, N≡N. On the otherhand, phosphorus because of its large size and small electronegativity does not show any tendency to form multiple bonds and therefore, diatomic molecule like P≡≡P is not formed. Instead, it prefers to form stable tetra atomic, P_4 molecules in which each P is linked to three other P atoms by three single covalent bonds. The four atoms in P_4 molecule lie at the corners of a regular tetrahedron.

Q.2. H_3PO_2 and H_3PO_3 act as good reducing agents but H_3PO_4 does not. Why?

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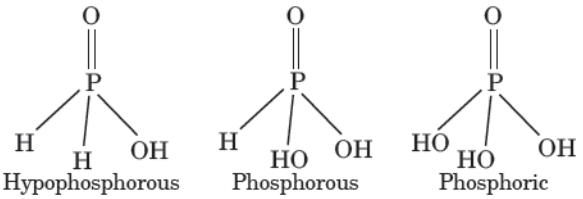
Ans. The structures of H_3PO_2, H_3PO_3 and H_3PO_4 are:



Hypophosphorous acid (H_3PO_2) | Phosphorous acid (H_3PO_3) | Phosphoric acid (H_3PO_4)

Due to the presence of P—H bonds, both H_3PO_2 and H_3PO_3 act as reducing agents. On the other hand, H_3PO_4 does not have any P—H bond and hence it does not act as a reducing agent.

Q.3. Why is nitrous oxide called laughing gas ?

Ans. When nitrous oxide (N_2O) is inhaled in minor quantities, it causes hysterical laughter and therefore, it is called laughing gas.

Q.4. What is the action of heat on

(*i*) Pyrophosphoric acid

(*ii*) Metaphosphoric acid

(*iii*) Phosphorous acid

Ans. (*i*) Pyrophosphoric acid ($H_4P_2O_7$) on heating gives metaphosphoric acid.

$$\underset{}{H_4P_2O_7} \xrightarrow{\Delta} \underset{\text{Metaphosphoric acid}}{2HPO_3} + H_2O$$

(*ii*) Metaphosphoric acid (HPO_3) on heating gives phosphorus pentoxide.

$$2HPO_3 \longrightarrow \underset{\text{Phosphorus pentaoxide}}{P_2O_5} + H_2O$$

(*iii*) Phosphorous acid (H_3PO_3) on heating gives phosphine and phosphoric acid.

$$\underset{}{4H_3PO_3} \xrightarrow{200°C} \underset{\text{Phosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3}$$

Q.5. What structures does PCl_5 adopt in the solid state and vapour state ?

Ans. In the solid state PCl_5 is ionic compound consisting of $[PCl_4]^+$ (tetrahedral) and $[PCl_6]^-$ (octahedral) ions. In vapour state, PCl_5 is monomeric having trigonal bipyramidal geometry.

Q.6. A translucent white waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B). Allotrope (A) on reaction with very dilute aqueous KOH liberates a highly poisonous gas (C) having rotten fish smell. With excess of chlorine forms (D) which hydrolyses to compound (E). Identify compounds (A) to (E).

Ans. (A) The white waxy solid (A) is white phosphorus.

When white phosphorus is heated in an inert atmosphere at 573K, it changes to red phosphorus.

(B) is red phosphorus.

(A) on heating with KOH liberates phosphine (C) which is poisonous gas with rotten fish smell.

$$P_4 + 3KOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + 3KH_2PO_2$$
(C)

White phosphorus (P_4) burns with excess of Cl_2 to form phosphorus pentachloride (D).

$$P_4 + 10Cl_2 \xrightarrow{\text{heat}} \underset{}{4PCl_5}$$
(D)

Hydrolysis of (D) gives phosphoric acid (E).

$$PCl_5 + 4H_2O \longrightarrow \underset{}{H_3PO_4} + 5HCl$$
(E)

Q.7. When a mixture of ammonium chloride and potassium dichromate are heated, a stable colourless gas (A) was evolved which did not support combustion but magnesium continued to burn in it. The gas (A) reacted with calcium carbide in an electric furnance forming a solid (B). The compound (B) was slowly hydrolysed by water forming an insoluble substance (C) and the solution of substance (D) which turned Nessler's reagent brown. Identify (A) to (E) and give the reactions involved.

Ans. (*i*) $K_2Cr_2O_7 + 2NH_4Cl \longrightarrow \underset{\text{Ammoniumdichromate}}{(NH_4)_2Cr_2O_7} + 2KCl$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} \underset{\text{(A)}}{N_2} + Cr_2O_3 + 4H_2O$$

N_2 does not support combustion but Mg burns in it

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

(*ii*) Gas (A) reacted with CaC_2

$$CaC_2 + N_2 \xrightarrow{\text{Heat}} \underset{\text{(B)}}{CaCN_2}$$

Calcium cyanamide

$$CaCN_2 + 3H_2O \longrightarrow \underset{\text{(C)}}{CaCO_3} + \underset{\text{(D)}}{2NH_3}$$

(*iii*) D reacts with Nessler's reagent to give borwn colour as

$$NH_3 + 2K_2HgI_4 + 3KOH \longrightarrow H_2NHgOHgI + 7KI + 2H_2O$$

Nessler's reagent — Brown ppt.

Q.8. When conc. H_2SO_4 was added to an unknown salt present in a test tube, a brown gas (A) was evolved. The gas intensified when copper turnings were also added into this test tube. On cooling the gas A changed into a colourless gas (B).

(*i*) Identify the gases (A) and (B).

(*ii*) Write the equations for the reactions involved.

Ans. The given salt is a nitrate salt which on reaction with conc. H_2SO_4 gives first vapours of HNO_3 which decompose to give brown gas (NO_2).

$$2NaNO_3 + H_2SO_4 \xrightarrow{\text{Heat}} \underset{\text{Colourless}}{Na_2SO_4 + 2HNO_3}$$

$$4HNO_3 \xrightarrow{\text{Heat}} \underset{\text{Brown gas}}{4NO_2} + 2H_2O + O_2$$
(A)

The gas intensified when copper turnings were added due to reduction of HNO_3 by Cu.

$$Cu + 4HNO_3 \xrightarrow{\text{Heat}} Cu(NO_3)_2 + \underset{\text{Brown gas}}{2NO_2\uparrow} + 2H_2O$$
(A)

On cooling the gas A changes into a colourless gas (B), N_2O_4.

$$\underset{\text{(A)}}{2NO_2} \rightleftharpoons \underset{\text{(B)}}{N_2O_4}$$

Q.9. Why does NCl_3 on hydrolysis give NH_3 and HOCl while PCl_3 on hydrolysis gives H_3PO_3 and HCl.

Ans. This is because N does not have *d*-orbitals to accommodate the electrons donated by O of water. Therefore, attack of H_2O occurs on Cl atom which has *d*-orbitals to accommodate the extra electrons donated by H_2O. As a result, Cl—O bond is formed leading to the formation of NH_3 and HOCl.

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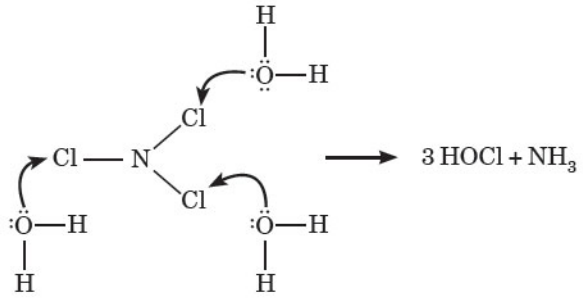
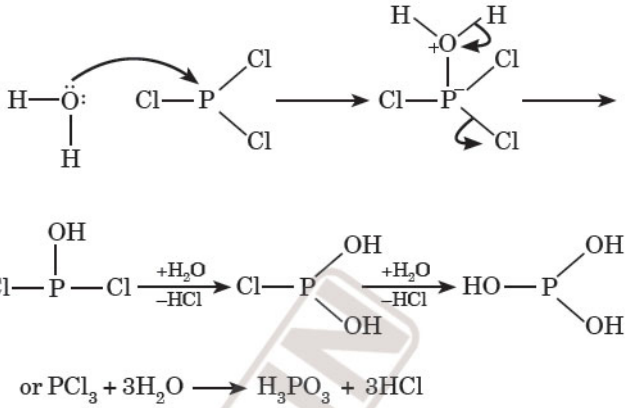


On the other hand, P and Cl both have *d*-orbitals to accommodate electrons donated by H_2O. But P—O bond is much stronger than Cl—O bond. Therefore, attack of H_2O molecules occur preferentially on P of PCl_3 to form H_3PO_3 and HCl.



Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Why is yellow phosphorus kept under water ?
2. Give one example in which ammonia acts as an oxidising agent.
3. Which one of PCl_4^+ and PCl_4^- is not likely to exist and why? *(D.S.B. 2012)*
4. NH_3 has higher boiling point than PH_3. *(Chhatisgarh S.B. 2013)*
5. Mention the basicity of H_3PO_2. *(Assam S.B. 2016)*
6. Write the disproportionation reaction of H_3PO_3. *(Assam S.B. 2013)*
7. What is the covalency of nitrogen in N_2O_5 ? *(D.S.B. 2013)*
8. Draw the structure of H_3PO_2 and explain why it is monobasic. *(Mizoram S.B. 2014)*
9. What is the basicity of H_3PO_4? *(D.S.B. 2015)*
10. Why is Bi(V) a stronger oxidant than Sb(V) ? *(A.I.S.B. 2008; D.S.B. 2009)*
11. Nitrogen is relatively inert as compared to phosphorus. Why ? *(A.I.S.B. 2010)*
12. Which is stronger reducing agent; SbH_3 or BiH_3 and why? *(A.I.S.B. 2012)*
13. What is the basicity of H_3PO_3 and why ? *(A.I.S.B. 2013, 2014)*
14. Why does NH_3 act as a Lewis base? *(A.I.S.B. 2014)*
15. Why does NO_2 dimerise? *(A.I.S.B. 2014)*
16. Out of white phosphorus and red phosphorus, which one is more reactive and why? *(A.I.S.B. 2015)*
17. On heating $Pb(NO_3)_2$ a brown gas is evolved which undergoes dimerization on cooling. Identify the gas. *(A.I.S.B. 2016)*
18. Write the formula of the compound of sulphur which is obtained when conc. HNO_3 oxidises S_8. *(A.I.S.B. 2017)*
19. Write the formula of the compound of phosphorus which is obtained when conc. HNO_3 oxidises P_4. *(A.I.S.B. 2017)*
20. Write the formula of the compound of iodine which is obtained when conc. HNO_3 oxidises I_2. *(A.I.S.B. 2017)*
21. Iodine is more soluble in KI than in water. Why? *(Karnataka S.B. 2018)*
22. Complete the following equation:
$$XeF_6 + H_2O \longrightarrow \ldots\ldots\ldots + 2HF$$
(Karnataka S.B. 2018)
23. N_2 is known whereas P_2 is not known. Why? *(Meghalaya S.B. 2018)*

Short Answer Questions *carrying 2 or 3 marks*

1. Describe the trends in the elements of group 15 in order of increasing atomic number:
   (*i*) Atomic radii (*ii*) Ionisation energy
   (*iii*) Oxidation state (*iv*) Catenation
2. Complete the following chemical reaction equations:
   (*i*) $P_4(s) + NaOH(aq) + H_2O(l) \longrightarrow$
   (*ii*) $BiCl_3 + H_2O \longrightarrow$
   (*iii*) $Cu + dil.HNO_3 \longrightarrow$
3. Draw the structures of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why ? *(D.S.B. 2010)*
4. State reasons for each of the following :
   (*i*) The N—O bond in NO_2^- is shorter than the N—O bond in NO_3^-.
   (*ii*) All the P–Cl bonds in PCl_5 molecule are not equivalent.
5. (*a*) Draw the shape of P_4O_{10}.
   (*b*) What happens when
   (*i*) PCl_5 is heated (*ii*) H_3PO_3 is heated ?
   Write the reactions involved. *(D.S.B. 2013)*

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6. (*a*) How is nitric acid manufactured by Ostwald process? Write the chemical equations involved. (*Mizoram S.B. 2014*)

(*b*) PCl_5 is known but PI_3 is not known. Why?

7. (*a*) Why does NH_3 act as a Lewis base?

(*b*) Bond angle in NH_4^+ is more than that in NH_3. (*H.P. S.B. 2014*)

8. Account for the following:

(*a*) PCl_5 is more covalent than PCl_3.

(*b*) Bi(V) is a stronger oxidizing agent than Sb(V).

(*c*) N—N single bond is weaker than P—P single bond.

9. (*a*) Write equations for the manufacture of HNO_3 by Ostwald process.

(*b*) Write the structural difference between white phosphorus and red phosphorus. (*D.S.B. 2014*)

(*c*) Molecular nitrogen is chemically very inert. Explain why? (*H.P.S.B. 2015*)

10. Write short notes on various allotropes of phosphorus.

Or

Name any five oxoacids of phosphorus and write their formulae. (*Hr.S.B. 2015*)

11. Explain the following:

(*a*) Why does PCl_3 fume in moisture?

(*b*) NO_2 dimerises to N_2O_4. (*Hr.S.B. 2015*)

12. (*a*) Give two methods of preparation of NH_3 and three important uses of NH_3.

(*b*) (*i*) NH_3 is a strong base but NF_3 does not show any basic property. Why?

(*ii*) What is laughing gas?

13. (*a*) Why does bond angle decrease in the hydrides of nitrogen family while going down the group?

(*b*) Why is ammonia more basic than phosphine?

(*c*) H_3PO_2 is monoprotic acid. Explain.

14. (*a*) Complete the following reactions:

(*i*) $PH_4I + NaOH \longrightarrow$ (*ii*) $P_4 + SO_2Cl_2 \longrightarrow$

(*iii*) NH_3(excess) + $Cl_2 \longrightarrow$

(*b*) Draw the structural formula of H_3PO_2. How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure?

15. (*a*) Draw the structure of H_3PO_4.

(*b*) Why does phosphorus exist as P_4 and nitrogen exists as N_2 gas?

16. (*a*) Write the principle for the production of NH_3 in Haber's process.

(*b*) What happens when ammonia reacts with

(*i*) Na (*ii*) CO_2 (*Jharkhand S.B. 2016*)

17. (*a*) Discuss the structure of PF_5.

(*b*) What are main reasons for anomalous properties of nitrogen ?

(*c*) How will you prepare HNO_3 by Ostwald process? (*Hr. S.B. 2017, Nagaland S.B. 2017*)

18. (*a*) Name *three* oxy-acids of phosphorus and draw their structures.

(*b*) Discuss the anomalous behaviour of oxygen. (*Hr.S.B. 2017*)

19. (*a*) PH_3 has lower boiling point than NH_3, explain why?

(*b*) Why does PCl_3 fume in moisture?

20. Give reasons for the following:

(*a*) NH_3 acts as a Lewis base.

(*b*) NO_2 dimerises.

21. Prepare a short write-up on PCl_3 and PCl_5 highlighting the preparation and chemical properties of PCl_3 and strucrture of PCl_5. (*Kerala S.B. 2017*)

22. (*a*) Complete the following reactions :

(*i*) $NH_3 + 3Cl_2$ (excess) $\longrightarrow$ (*ii*) $NaN_3 \xrightarrow{\text{Heat}}$

Or

What happens when

(*i*) $(NH_4)_2Cr_2O_7$ is heated?

(*ii*) H_3PO_3 is heated?

Write the equations. (*D.S.B. 2017*)

(*b*) Draw the structures of the following :

(*i*) $H_4P_2O_7$

(*ii*) HNO_3 (*D.S.B. 2017*)

23. How would you account for the following:

(*i*) NCl_3 is an endothermic compound while NF_3 is an exothermic one.

(*ii*) Where R is an alkyl group $R_3P = O$ exists but $R_3N = O$ does not.

(*iii*) At room temperature, N_2 is much less reactive. (*A.I.S.B. 2013*)

24. Give reasons for the following :

(*i*) BiH_3 is the strongest reducing agent amongst all the hydrides of group 15 elements. (*A.I.S.B. 2013*)

(*ii*) Though nitrogen exhibits +5 oxidation state, it does not form pentahalide.

(*iii*) $(CH_3)_3P = O$ exists but $(CH_3)_3N = O$ does not.

(*iv*) H_3PO_2 is a stronger reducing agent that H_3PO_3. (*A.I.S.B. 2014*)

25. Assign reason for the following:

(*i*) H_3PO_2 is a stronger reducing agent than H_3PO_4.

(*ii*) Red phosphorus is less reactive than white phosphorus.

(*iii*) N_2O_5 is more acidic than N_2O_3. (*A.I.S.B. 2017*)

Long Answer Questions *carrying 5 marks*

1. (*a*) Write down the steps involved in the manufacture of HNO_3 by Ostwald process.

(*b*) Write the structural formula of PCl_5 in solid state and also indicate the hybridisation of phosphorus atoms.

(*c*) What happens, when sulphur is treated with conc. HNO_3? (*Meghalaya S.B. 2014*)

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2. Explain the following facts—
(*i*) NH_3 forms hydrogen bond but PH_3 does not.
(*ii*) NH_3 is more basic than BiH_3.
(*iii*) PH_3 has lower boiling point than NH_3.

3. Explain Ostwald process for manufacturing nitric acid. Draw structure of nitric acid and write its uses also.

Or

(*a*) Why does reactivity of nitrogen differ from phosphorus?
(*b*) What happens when zinc reacts with
(*i*) concentrated HNO_3 (*ii*) dilute HNO_3
(*c*) Write formula of phosphine. *(Hr. S.B. 2013)*

4. (*a*) Describe the manufacture of ammonia by Haber's process with favourable conditions.
(*b*) State the hybridisation of the central atom and draw the structure of PCl_3.
(*c*) Why is H_3PO_4 tribasic and H_3PO_3 dibasic?

5. (*a*) Which allotrope of phosphorus is more reactive and why?
(*b*) Why does nitric acid act as an oxidising agent? How it oxidises
(*i*) carbon to carbonic acid
(*ii*) sulphur dioxide to sulphuric acid.
(*iii*) sulphur to sulphuric acid.
(*iv*) ferrous sulphate to ferric sulphate.

6. (*a*) Arrange the following in the increasing order of property mentioned:
(*i*) H_3PO_3, H_3PO_4, H_3PO_2 (Reducing character)
(*ii*) NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Base strength) *(D.S.B. 2016)*
(*b*) Why is H_3PO_3 diprotic in nature? Draw structure.

7. (*a*) Give a laboratory method of preparation of dinitrogen. *(Assam S.B. 2017)*
(*b*) Unlike phosphorus, nitrogen shows little tendency for catenation. Why?
(*c*) Complete the following chemical equations

(*i*) $Mg + N_2 \xrightarrow{heat}$ .....

(*ii*) $Ba(N_3)_2 \xrightarrow{decomposition}$ ..... + ...

(*iii*) $(NH_4)_2Cr_2O_7 \xrightarrow{heat}$ ..... + ... H_2O

(Assam S.B. 2017)

8. (*a*) Explain why HNO_2 behaves both as oxidising as well as reducing agent. *(Assam S.B. 2017)*

Or

(*b*) Draw the structure of H_3PO_2. How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure ?
(*c*) What happens when $(NH_4)_2Cr_2O_7$ is heated?
(*d*) How does ammonia react with a solution of Cu^{2+}?

9. (*a*) Nitric acid forms an oxide of nitrogen on reaction with P_4. Write the formula of the stable molecule formed when this oxide undergoes dimerisation.
(*b*) Write the disproportionation reaction of the oxoacid of nitrogen in which nirtogen is in +3 oxidation state.
(*c*) Draw the molecular structures of the following compounds :
(*i*) N_2O_5 (*ii*) H_3PO_2
(*d*) Account for the following:
(*i*) N_2 is less reactive at room temperature.
(*ii*) Reducing character decreases from NH_3 to BiH_3.
(*e*) Which poisonous gas is evolved when white phosphorus is heated with conc. NaOH solution? Write the chemical equations involved.

Hints & Answers *for* Revision Exercises

Very Short Answer Questions

1. Because it catches fire in air.

3. PCl_4^- is not likely to exist because lone pair on P in PCl_3 can be donated to Cl^+ and not to Cl^-.

4. NH_3 forms hydrogen bonds but PH_3 does not.

5. one **6.** $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$

7. Five **9.** tribasic (3)

12. BiH_3 because BiH_3 is less stable than SbH_3 because of larger size of Bi than Sb.

13. Two, because it contains two P–OH bonds and therefore, can give two H^+ ions.

16. White P is more reactive because of angular strain in P_4 molecules where the angles are only 60°

17. NO_2

$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$

$2NO_2 \xrightarrow{Cool} N_2O_4$

18. H_3PO_4 **19.** H_2SO_4 **20.** HIO_3

21. Iodine combines with KI to form a soluble complex.
$KI + I_2 \longrightarrow KI_3$ (soluble)

22. XeF_6
$XeF_4 + O_2F_2 \xrightarrow{143K} XeF_6 + O_2$

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Competition File

Objective Questions

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions *M. C. Q.*

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answer :

A1. The brown gas formed when HNO_3 is reduced by metals is
(a) N_2O (b) N_2O_3
(c) NO_2 (d) NO.

A2. The hydride of group 15 having largest bond angle is :
(a) NH_3 (b) PH_3
(c) AsH_3 (d) BiH_3.

A3. The oxoacid of P having oxidation state + 4 is :
(a) Phosphorus acid
(b) Hypophosphoric acid
(c) Phosphoric acid
(d) Metaphosphoric acid.

A4. Nitric acid (conc.) oxidises phosphorus to
(a) H_3PO_4 (b) P_2O_5
(c) H_3PO_3 (d) $H_4P_2O_7$.

A5. Ammonia gas can be dried over
(a) $CaCl_2$ (b) Conc. H_2SO_4
(c) PCl_5 (d) Quick lime

A6. Of the following hydrides which is the strongest reducing agent ?
(a) NH_3 (b) SbH_3
(c) AsH_3 (d) PH_3.

A7. Pure nitrogen gas is obtained from
(a) $NH_3 + NaNO_2$
(b) $NH_4Cl + NaNO_2$
(c) $N_2O + Cu$
(d) $(NH_4)_2Cr_2O_7$.

A8. Calcium phosphide gets hydrolysed and gives
(a) $Ca_3(PO_4)_2$
(b) PH_3
(c) H_3PO_4
(d) $(HPO_3)_n$

A9. Which of the following is a coloured gas ?
(a) NO_2 (b) N_2O_5
(c) N_2O_4 (d) N_2O.

A10. The oxide of nitrogen obtained by dehydration of nitric acid with phosphorus pentoxide is
(a) NO_2 (b) N_2O_5
(c) N_2O_4 (d) N_2O.

A11. Which compound of nitrogen is formed when $CaCN_2$ reacts with hot water ?
(a) NH_3
(b) N_2O
(c) NH_2NH_2
(d) NO_2.

A.12. Among the trihalides of nitrogen, which one is least basic ?
(a) NF_3
(b) NCl_3
(c) NBr_3
(d) NI_3.

A13. On heating ammonium dichromate, the gas evolved is
(a) Oxygen
(b) Ammonia
(c) Nitric acid
(d) Nitrogen.

A14. Which of the following is not correct : White phosphorus (P_4) has
(a) six P—P single bonds
(b) four P—P single bonds
(c) four lone pairs of electrons
(d) PPP angle is 60°.

A15. The number of P—O—P bonds in cyclic metaphosphoric acid is
(a) zero
(b) two
(c) three
(d) four.

A16. The number of σ–bonds in P_4O_{10} is
(a) 6 (b) 16
(c) 20 (d) 7.

Answers

A1. (c) **A2.** (a) **A3.** (b) **A4.** (a) **A5.** (d) **A6.** (b) **A7.** (b) **A8.** (b) **A9.** (a)
A10. (b) **A11.** (a) **A12.** (a) **A13.** (d) **A14.** (b) **A15.** (c) **A16.** (b).

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B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

AIPMT & Other State Boards' Medical Entrance

B1. Which of the following statements is not valid for oxoacids of phosphorus?
(*a*) Orthophosphoric acid is used in the manufacture of triple superphosphate.
(*b*) Hypophosphorous acid is a diprotic acid.
(*c*) All oxoacids contain tetrahedral four coordinated phosphorus.
(*d*) All oxoacids contain at least one P = O unit and one P – OH group. *(A.I.P.M.T. 2012)*

B2. Strong reducing behaviour of H_3PO_2 is due to:
(*a*) High oxidation state of phosphorus
(*b*) Presence of two –OH groups and one P—H bond
(*c*) Presence of one –OH group and two P—H bonds
(*d*) High electron gain enthalpy of phosphorus
(AIPMT 2015)

B3. Nitrogen dioxide and sulphur dioxide have some properties in common. Which property is shown by one of these compounds, but not by the other?
(*a*) Is soluble in water.
(*b*) Is used as a food preservative.
(*c*) Forms 'acid–rain.
(*d*) Is a reducing agent. *(AIPMT 2015)*

B4. Which is the correct statement for the given acids?
(*a*) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid.
(*b*) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid.
(*c*) Both are diprotic acids.
(*d*) both are triprotic acids. *(NEET 2016)*

B5. The product obtained as a result of a reaction of nitrogen with CaC_2 is
(*a*) $CaCN_2$ (*b*) Ca_2CN
(*c*) $(CN)_2$ (*d*) CaCN
(NEET 2016)

B6. When copper is heated with conc. HNO_3 it produces
(*a*) $Cu(NO_3)_2$, NO and NO_2
(*b*) $Cu(NO_3)_2$ and N_2O
(*c*) $Cu(NO_3)_2$ and NO_2
(*d*) $Cu(NO_3)_2$ and NO *(NEET 2016)*

B7. The correct order of N-compounds in its decreasing order of oxidation states is
(*a*) HNO_3, NO, N_2, NH_4Cl
(*b*) HNO_3, NO, NH_4Cl, N_2
(*c*) HNO_3, NH_4Cl, NO, N_2
(*d*) NH_4Cl, N_2, NO, HNO_3 *(NEET 2018)*

B8. Chlorine reacts with excess of ammonia to form
(*a*) NH_4Cl (*b*) $N_2 + HCl$
(*c*) $N_2 + NH_4Cl$ (*d*) $N_2 + NCl_3$
(*e*) $NCl_3 + HCl$ *(Kerala P.M.T. 2007)*

B9. Which of the following is the correct order of increasing enthalpy of vaporisation ?
(*a*) $NH_3 < PH_3 < AsH_3$ (*b*) $AsH_3 < PH_3 < NH_3$
(*c*) $PH_3 < AsH_3 < NH_3$ (*d*) $NH_3 < AsH_3 < PH_3$
(*e*) $AsH_3 < NH_3 < PH_3$ *(Kerala P.M.T. 2007)*

B10. The maximum number of P–H bonds are contained in which of the following molecules?
(*a*) H_3PO_2 (*b*) H_3PO_3
(*c*) H_3PO_4 (*d*) $H_4P_2O_7$
(A.M.U. Med 2010)

B11. The basicity of pyrophosphorous acid is
(*a*) 2 (*b*) 4 (c) 1
(*d*) 5 (*e*) 3 *(Kerala PMT 2011)*

B12. The oxidation state of phosphorus in cyclotrimetaphosphoric acid is
(*a*) + 3 (*b*) + 5 (c) – 3
(*d*) + 2 (*e*) – 2 *(Kerala PMT 2011)*

B13. The *p*-block element that forms predominantly basic oxide is
(*a*) N (*b*) P
(*c*) As (*d*) Sb
(*e*) Bi *(Kerala P.M.T. 2012)*

B14. The oxoacid of phosphorus that reduces silver nitrate into metallic silver is
(*a*) H_3PO_2 (*b*) $H_4P_2O_6$ (*c*) H_3PO_4
(*d*) $H_4P_2O_7$ (*e*) $(HPO_3)_n$ *(Kerala PMT 2015)*

B15. Which of the following oxides of nitrogen contains N—O—N bond?
(*a*) Dinitrogen oxide (*b*) Nitrogenmonoxide
(*c*) Dinitrogen pentoxide (*d*) Dinitrogentrioxide
(*e*) Dinitrogen tetroxide (*e*) 2.46
(Kerala PMT 2015)

JEE (Main) & Other State Boards' Engineering Entrance

B16. Three reactions involving $H_2PO_4^-$ are given below :
(*i*) $H_3PO_4 + H_2O \longrightarrow H_3O^+ + H_2PO_4^-$
(*ii*) $H_2PO_4^- + H_2O \longrightarrow HPO_4^{2-} + H_3O^+$
(*iii*) $H_2PO_4^- + OH^- \longrightarrow H_3PO_4 + O^{2-}$
In which of the above does $H_2PO_4^-$ act as an acid ?
(*a*) (*iii*) only (*b*) (*i*) only
(*c*) (*ii*) only (*d*) (*i*) and (*ii*)
(A.I.E.E.E 2010)

Answers

B1. (*b*) **B2.** (*c*) **B3.** (*b*) **B4.** (*a*) **B5.** (*a*) **B6.** (*c*) **B7.** (*a*) **B8.** (*a*) **B9.** (*a*)
B10. (*a*) **B11.** (*a*) **B12.** (*b*) **B13.** (*e*) **B14.** (*a*) **B15.** (*c*) **B16.** (*c*)

Competition File

B17. Which of the following statement is wrong ?
(*a*) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the periodic table.
(*b*) Nitrogen cannot form $d\pi$-$p\pi$ bond.
(c) Single N – N bond is weaker than the single P – P bond.
(*d*) N_2O_4 has two resonance structures.
(A.I.E.E.E. 2011)

B18. The reaction of zinc with dilute and concentrated nitric acid, respectively produces
(*a*) N_2O and NO_2 (*b*) NO and NO_2
(*c*) NO and N_2O (*d*) NO_2 and N_2O
(JEE Main 2016)

B19. The pair in which phosphorus atoms have a formal oxidation state of +3 is
(*a*) orthophosphorous and pyrophosphorous acids
(*b*) pyrophosphorous and hypophosphoric acids
(*c*) orthophosphorous and hypophosphoric acids
(*d*) pyrophosphorous and pyrophosphoric acids.
(JEE Main 2016)

B20. The compound that does not produce nitrogen gas by the thermal decomposition is:
(*a*) $Ba(N_3)_2$ (*b*) $(NH_4)_2Cr_2O_7$
(c) NH_4NO_2 (*d*) $(NH_4)_2SO_4$
(JEE Main 2018)

B21. Which of the following contains P — O — P bond ?
(*a*) Hypophosphorous acid (*b*) Phosphorus acid
(*c*) Pyrophosphoric acid (*d*) Orthophosphoric acid

B22. NO_2 is not obtained on heating
(*a*) $AgNO_3$ (*b*) KNO_3
(c) $Cu(NO_3)_2$ (*d*) $Pb(NO_3)_2$
(W.B. JEE 2011, 2016)

B23. The least stable hydride of 15th group elements is
(*a*) NH_3 (*b*) PH_3
(c) AsH_3 (*d*) SbH_3
(*e*) BiH_3 *(Kerala PET 2011)*

B24. Pick out the wrong statement.
(*a*) Nitrogen has the ability to form $p\pi$-$p\pi$ bonds with itself.
(*b*) Bismuth forms metallic bonds in elemental state.
(c) Catenation tendency is higher in nitrogen when compared with other elements of the same group.
(*d*) Nitrogen has higher first ionisation enthalpy when compared with other elements of the same group.
(*e*) Arsenic forms $d\pi$-$d\pi$ bonds with transition metals.
(Kerala P.E.T. 2012)

B25. Nitric acid can be obtained from ammonia via the formation of the intermediate compounds
(*a*) nitric oxide and nitrogen dioxide
(*b*) nitrogen and nitric oxide
(*c*) nitric oxide and dinitrogen pentoxide
(*d*) nitrogen and nitrous oxide
(W.B.J.E.E. Engg. 2013)

B26. An inorganic salt (A) is decomposed on heating to give two products (B) and (C). Compound (C) is a liquid at room temperature and is neutral to litmus while the compound (B) is a colourless neutral gas. Compounds (A), (B) and (C) are
(*a*) NH_4NO_3, N_2O, H_2O (*b*) NH_4NO_2, NO, H_2O
(*c*) CaO, H_2O, $CaCl_2$ (*d*) $Ba(NO_3)_2$, H_2O, NO_2
(*e*) $Mg(NO_3)_2$, N_2O_5, H_2O *(Kerala P.E.T. 2013)*

B27. Oxyacids of phosphorous and the starting materials for their preparation are given below :

Oxyacid	–	**Materials for preparation**
(A) H_3PO_2	–	(*i*) Red P + alkali
(B) H_3PO_3	–	(*ii*) $P_4O_{10} + H_2O$
(C) H_3PO_4	–	(*iii*) $P_2O_3 + H_2O$
(D) $H_4P_2O_6$	–	(*iv*) White P + alkali

Choose the correct answer from the codes given below:
(*a*) (A) – (*iv*); (B) – (*iii*); (C) – (*ii*); (D) – (*i*)
(*b*) (A) – (*i*); (B) – (*iii*); (C) – (*ii*); (D) – (*iv*)
(*c*) (A) – (*iv*); (B) – (*iii*); (C) – (*i*); (D) – (*ii*)
(*d*) (A) – (*ii*); (B) – (*iii*); (C) – (*i*); (D) – (*iv*)
(*e*) (A) – (*iii*); (B) – (*i*); (C) – (*ii*); (D) – (*iv*)
(Kerala P.E.T. 2013)

B28. The statement that is not correct is
(*a*) Hypophosphorous acid reduces silver nitrate to silver
(*b*) In solid state PCl_5 exists as $[PCl_4]^+$ $[PCl_6]^-$
(*c*) Pure phosphine is non-inflammable
(*d*) Phosphorous acid on heating disproportionates to give metaphosphoric acid and phosphine.
(Karnataka CET 2014)

B29. On heating with concentrated NaOH solution in an inert atmosphere of CO_2, white phosphorus gives a gas. Which of the following statements is incorrect about the gas?
(*a*) It is more basic than NH_3.
(*b*) Its solution in water decomposes in the presence of light.
(*c*) It is less basic than NH_3.
(*d*) It is highly poisonous and has smell like rotten fish. *(Karnataka CET 2015)*

B30. What is the basicity of orthophosphorus acid?
(*a*) One (*b*) Two
(*c*) Three (*d*) Four *(MH-CET 2015)*

B31. In the solid state, PCl_5 exists as
(*a*) $[PCl_4]^-$ and $[PCl_6]^+$ ions
(*b*) covalent PCl_5 molecules only
(*c*) $[PCl_4]^+$ and $[PCl_6]^-$ ions
(*d*) covalent P_2Cl_{10} molecules only. *(WB JEE 2016)*

B32. Thermal decomposition of ammonium dichromate gives
(*a*) N_2, H_2O and Cr_2O_3 (*b*) N_2, NH_3 and CrO
(*c*) $(NH_4)_2CrO_4$ and H_2O (*d*) N_2, H_2O and CrO_3
(Kerala PET 2016)

Answers

B17. (*a*)	**B18.** (*a*)	**B19.** (*a*)	**B20.** (*d*)	**B21.** (*c*)	**B22.** (*b*)	**B23.** (*e*)	**B24.** (*c*)	**B25.** (*a*)
B26. (*a*)	**B27.** (*a*)	**B28.** (*d*)	**B29.** (*a*)	**B30.** (*b*)	**B31.** (*c*)	**B32.** (*a*)		

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B33. Which is true regarding nitrogen?
(a) Less electronegative
(b) Has low ionisation enthalpy
(c) *d*-orbitals are available
(d) Ability to form $p\pi$–$p\pi$ bonds with itself
(Karnataka C.E.T. 2016)

B34. What will be the resultant products formed when the phosphorus halide, PBr_5 splits up?
(a) $[PBr_4]^+$ and Br^- (b) $[PBr_6]^-$ and $[PBr_4]^+$
(c) $[PBr_4]^+$ (d) $[PBr_6]^-$
(J.K. CET 2018)

B35. Maximum number of covalent bonds formed by N and P are
(a) 3, 5 (b) 3, 6
(c) 3, 4, 5 (d) 3, 4, 6
(Kerala PET 2018)

B36. Consider the following compounds
1. $(NH_4)_2Cr_2O_7$ 2. NH_4NO_2
3. NH_4VO_3 4. NH_4NO_3
Which compound(s) yield nitrogen gas upon heating?
(a) 1 and 2 (b) 2 and 3
(c) 3 and 4 (d) 1 and 4
(e) All *(Kerala PET 2018)*

B37. Very pure N_2 can be obtained by
(a) thermal decomposition of ammonium dichromate
(b) treating aqueous solution of NH_4Cl and $NaNO_2$
(c) liquefaction and fractional distillation of liquid air
(d) thermal decompositon of sodium azide
(Karnataka C.E.T. 2018)

B38. Good reducing nature of H_3PO_2 is attributed to the presence of
(a) One P—OH bond (b) One P—H bond
(c) Two P—H bonds (d) Two P—OH bonds
(JEE Main 2019)

B39. The pair that contains two P—H bonds in each of the oxoacids is
(a) H_3PO_2 and $H_4P_2O_5$ (b) $H_4P_2O_5$ and $H_4P_2O_6$
(c) H_3PO_3 and H_3PO_2 (d) $H_4P_2O_5$ and H_3PO_3
(JEE Main 2019)

JEE (Advance) for IIT Entrance

B40. The reaction of P_4 with X leads selectively to P_4O_6. The X is
(a) Dry O_2
(b) A mixture of O_2 and N_2
(c) Moist O_2
(d) O_2 in the presence of aqueous NaOH *(I.I.T. 2009)*

B41. Extra pure N_2 can be obtained by heating
(a) NH_3 with CuO (b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$ *(I.I.T. JEE 2011)*

B42. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively.
(a) redox reaction; – 3 and – 5
(b) redox reaction; + 3 and + 5
(c) disproportionation reaction; – 3 and + 5
(d) disproportionation reaction; – 3 and + 3
(I.I.T. J.E.E. 2012)

B43. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of
(a) NO (b) NO_2
(c) N_2O (d) N_2O_4
(J.E.E. Advance 2013)

B44. The order of the oxidation state of the phosphorus atom in H_3PO_2, H_3PO_4, H_3PO_3, and $H_4P_2O_6$ is
(a) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$
(b) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$
(c) $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$
(d) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$
(JEE Advance 2017)

Answers

B33. (d) **B34.** (a) **B35.** (a) **B36.** (a) **B37.** (d) **B38.** (c) **B39.** (a) **B40.** (b) **B41.** (d)
B42. (c) **B43.** (b) **B44.** (d)

C MULTIPLE CHOICE QUESTIONS *with more than one correct answers*

C1. White phosphorus has
(a) four P—P bonds (b) bond angle $\angle PPP = 60°$
(c) six P—P bonds (d) polymeric structure.

C2. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after some time. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are)
(a) NH_4NO_3 (b) NH_4NO_2
(c) NH_4Cl (d) $(NH_4)_2SO_4$ *(I.I.T. 2008)*

C3. Nitrogen oxide(s) that contain(s) N—N bond(s) is (are)
(a) N_2O (b) N_2O_3
(c) N_2O_4 (d) N_2O_5
(I.I.T. JEE 2009)

C4. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}
(a) can also be prepared by reaction of P_4 and HNO_3
(b) is diamagnetic
(c) contains one N—N bond
(d) reacts with Na metal producing brown gas.
(JEE Advance 2016)

C5. White phosphorus P_4 has the following characteristics
(a) 6 P – P single bonds
(b) 4 P – P single bonds
(c) 4 lone pair of electrons
(d) P – P – P angle of 60° *(WB JEE 2018)*

Answers

C1. (b), (c) **C2.** (a), (b) **C3.** (a), (b), (c) **C4.** (b), (d) **C5.** (a), (c), (d)

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C6. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300 °C is (are)

(*a*) NH_4NO_3 (*b*) $(NH_4)_2Cr_2O_7$

(*c*) $Ba(N_3)_2$ (*d*) Mg_3N_2

(JEE Advance 2018)

C7. Based on the compounds of group 15 elements, the correct statement(s) is (are)

(*a*) Bi_2O_5 is more basic than N_2O_5

(*b*) NF_3 is more covalent than BiF_3

(*c*) PH_3 boils at lower temperature than NH_3

(*d*) the N–N single bond is stronger than the P–P single bond. *(JEE Advance 2018)*

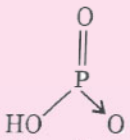
Answers

C6. (*b*), (*c*) **C7.** (*a*), (*b*), (*c*)

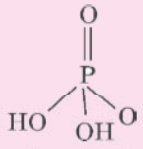
D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage I.

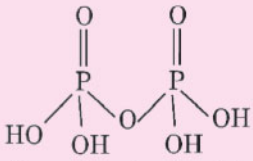
Phosphorus forms a variety of oxyacids. In all these, phosphorus is sp^3 hybridised and is tetrahedrally bonded to four neighbouring atoms. These contain P—OH bonds, the hydrogen of which are ionisable giving acidic character to these compounds. These also contain P—H bonds in which hydrogens are not ionisable because P and H have nearly same electronegativity. The presence of P—H group in these oxyacids is responsible for their reducing properties. The structures of some oxyacids are given below :



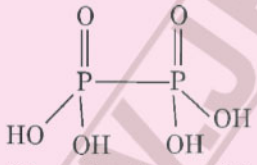
meta-Phosphoric acid (A)



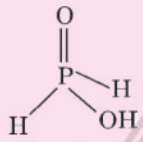
ortho-phosphoric acid (B)



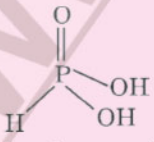
Pyrophosphoric acid (C)



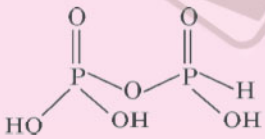
Hypophosphoric acid (D)



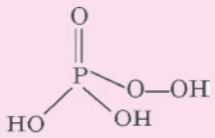
Hypophosphorus acid (E)



Phosphorus acid (F)



Pyrophosphorous acid (G)



Peroxomonophosphoric acid (H)

Answer the following questions :

D1. The oxyacid of P having tetrabasicity is/are

(*a*) C and H (*b*) C and E

(*c*) C and D (*d*) B and E

D2. Which of the acids show reducing properties ?

(*a*) E, F and G (*b*) E, G and H

(*c*) E only (*d*) E and F

D3. Monobasic oxyacids of phosphorus is/are

(*a*) H and E (*b*) A and E

(*c*) C and G (*d*) E only

D4. Which of these can exist as polymeric ?

(*a*) A and E (*b*) A only

(*c*) C and G (*d*) H only.

D5. Which of these is dibasic as well as reducing ?

(*a*) E (*b*) A

(*c*) G (*d*) F.

Passage II.

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorus.

Answer the following questions :

D6. Among the following, the correct statement is

(*a*) Phosphates have no biological significance in humans

(*b*) Between nitrates and phosphates, phosphates are less abundant in earth's crust

(*c*) Between nitrates and phosphates, nitrates are less abundant in earth's crust

(*d*) Oxidation of nitrates is possible in soil.

Answers

Passage I. **D1.** (*c*) **D2.** (*a*) **D3.** (*d*) **D4.** (*a*) **D5.** (*d*)

Passage II. **D6.** (*c*)

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D7. Among the following, the correct statement is
(*a*) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional.
(*b*) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(*c*) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(*d*) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional.

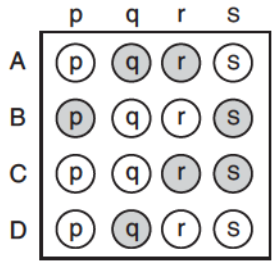
D8. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
(*a*) dimerization reaction
(*b*) disproportionation reaction
(*c*) condensation reaction
(*d*) precipitation reaction.

Answers

Passage II. **D7.** (*c*) **D8.** (*b*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.



If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the compound in Column I with the property in Column II.

Column I	Column II
(A) Pyrophosphoric acid	(*p*) Dibasic
(B) Thiosulphuric acid	(*q*) has oxidiation of +3 of central atom
(C) Orthophosphoric acid	(*r*) has +5 oxidation state of central atom
(D) Phosphoric acid	(*s*) tribasic

2. Match each of the reactions given in Column I with the corresponding product(s) given in Column II.

Column I	Column II
(A) Cu + dil. H_2SO_4	(*p*) NO
(B) Cu + conc. HNO_3	(*q*) NO_2
(C) Zn + dil. HNO_3	(*r*) N_2O
(D) Zn + conc. HNO_3	(*s*) $Cu(NO_3)_2$
	(*t*) $Zn(NO_3)_2$

(I.I.T. 2009)

Answers

(1) : (A) – (*r*) (B) – (*p*) (C) – (*r*), (*s*) (D) – (*p*), (*q*)
(2) : (A) – (*p*), (*s*) (B) – (*q*), (*s*) (C) – (*r*), (*t*) (D) – (*q*), (*t*)

Competition File

Integer Type Questions

Integer Type : The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. Total number of dibasic acids among H_3PO_4, $H_4P_2O_7$, $H_4P_2O_6$, H_3PO_5, H_3PO_3, $H_4P_2O_5$, H_3PO_2 is
2. Among phosphonic acid, phosphinic acid, pyrophosphorous acid, hypophosphorous acid, hypophosphoric acid, orthophosphoric acid, diphosphoric acid, metaphosphoric acid, peroxophosphoric acid, the acids having +3 oxidation state of P are
3. Among the following, the number of compounds that can react with PCl_5 to give $POCl_3$ is O_2, CO_2, SO_2, H_2O, H_2SO_4, P_4O_{10}. *(I.I.T. 2011)*
4. The difference between the number of lone pairs and P – O bonds in P_4O_6 molecule is
5. The total number of lone pairs of elections in N_2O_3 is *(JEE Advance 2015)*

Answers

1. 2. **2.** 2. **3.** 5 **4.** 4 **5.** 8

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. In a cyclotrimetaphosphoric acid molecule, how many single and double bonds are present?
   (*a*) 3 double bonds; 9 single bonds
   (*b*) 6 double bonds; 6 single bonds
   (*c*) 3 double bonds; 12 single bonds
   (*d*) Zero double bonds; 12 single bonds
2. Which of the following elements can be involved in pπ–dπ bonding?
   (*a*) Carbon (*b*) Nitrogen
   (*c*) Phosphorus (*d*) Boron
3. Bond dissociation enthalpy of E—H (E = element) bonds is given below. Which of the compounds will act as strongest reducing agent?

Compound	NH_3	PH_3	AsH_3	SbH_3
Δ_{diss} (E—H)/kJ mol^{-1}	389	322	297	255

   (*a*) NH_3 (*b*) PH_3
   (*c*) AsH_3 (*d*) SbH_3
4. On heating with concentrated NaOH solution in an inert atmosphere of CO_2, white phosphorus gives a gas. Which of the following statement is **incorrect** about the gas?
   (*a*) It is highly poisonous and has smell like rotten fish.
   (*b*) It's solution in water decomposes in the presence of light.
   (*c*) It is more basic than NH_3.
   (*d*) It is less basic than NH_3.
5. Which of the following acids forms three series of salts?
   (*a*) H_3PO_2 (*b*) H_3BO_3
   (*c*) H_3PO_4 (*d*) H_3PO_3
6. Strong reducing behaviour of H_3PO_2 is due to
   (*a*) Low oxidation state of phosphorus
   (*b*) Presence of two –OH groups and one P–H bond
   (*c*) Presence of one –OH group and two P–H bonds
   (*d*) High electron gain enthalpy of phosphorus
7. On heating lead nitrate forms oxides of nitrogen and lead. The oxides formed are _____.
   (*a*) N_2O, PbO (*b*) NO_2, PbO
   (*c*) NO, PbO (*d*) NO, PbO_2
8. Which of the following elements does not show allotropy?
   (*a*) Nitrogen (*b*) Bismuth
   (*c*) Antimony (*d*) Arsenic
9. Maximum covalency of nitrogen is _____.
   (*a*) 3 (*b*) 5
   (*c*) 4 (*d*) 6
10. Which of the following statements is wrong?
    (*a*) Single N–N bond is stronger than the single P–P bond.
    (*b*) PH_3 can act as a ligand in the formation of coordination compound with transition elements.
    (*c*) NO_2 is paramagnetic in nature.
    (*d*) Covalency of nitrogen in N_2O_5 is four.

Answers

1. (*a*) **2.** (*c*) **3.** (*d*) **4.** (*c*) **5.** (*c*) **6.** (*c*) **7.** (*b*) **8.** (*a*)
9. (*c*) **10.** (*a*)

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11. A brown ring is formed in the ring test for NO_3^- ion. It is due to the formation of
(a) $[Fe(H_2O)_5(NO)]^{2+}$ (b) $FeSO_4.NO_2$
(c) $[Fe(H_2O)_4(NO)_2]^{2+}$ (d) $FeSO_4.HNO_3$

12. Elements of group-15 form compounds in +5 oxidation state. However, bismuth forms only one well characterised compound in +5 oxidation state. The compound is
(a) Bi_2O_5 (b) BiF_5
(c) $BiCl_5$ (d) Bi_2S_5

13. On heating ammonium dichromate and barium azide separately we get
(a) N_2 in both cases
(b) N_2 with ammonium dichromate and NO with barium azide
(c) N_2O with ammonium dichromate and N_2 with barium azide
(d) N_2O with ammonium dichromate and NO_2 with barium azide

14. In the preparation of HNO_3, we get NO gas by catalytic oxidation of ammonia. The moles of NO produced by the oxidation of two moles of NH_3 will be _____.
(a) 2 (b) 3
(c) 4 (d) 6

15. The oxidation state of central atom in the anion of compound NaH_2PO_2 will be _____.
(a) +3 (b) +5
(c) +1 (d) –3

16. In solid state PCl_5 is a _____.
(a) covalent solid
(b) octahedral structure
(c) ionic solid with $[PCl_6]^+$ octahedral and $[PCl_4]^-$ tetrahedra
(d) ionic solid with $[PCl_4]^+$ tetrahedral and $[PCl_6]^-$ octahedra

II. Multiple Choice Questions (Type-II)

Note : *In the following questions two or more options may be correct.*

17. Which of the following is correct for P_4 molecule of white phosphorus?
(a) It has 6 lone pairs of electrons.
(b) It has six P–P single bonds.
(c) It has three P–P single bonds.
(d) It has four lone pairs of electrons.

18. Which of the following statements are correct?
(a) All the three N—O bond lengths in HNO_3 are equal.
(b) All P—Cl bond lengths in PCl_5 molecule in gaseous state are equal.
(c) P_4 molecule in white phohsphorus have angular strain therefore white phosphorus is very reactive.
(d) PCl_5 is ionic in solid state in which cation is tetrahedral and anion is octahedral.

Assertion and Reason Type Questions

Note : *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.*
(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
(c) Assertion is correct, but reason is wrong statement.
(d) Assertion is wrong but reason is correct statement.
(e) Both assertion and reason are wrong statements.

19. **Assertion :** N_2 is less reactive than P_4.
Reason : Nitrogen has more electron gain enthalpy than phosphorus.

20. **Assertion :** HNO_3 makes iron passive.
Reason : HNO_3 forms a protective layer of ferric nitrate on the surface of iron.

Answers

11. (a) **12.** (b) **13.** (a) **14.** (a) **15.** (c) **16.** (d) **17.** (c) **18.** (d) **19.** (c) **20.** (c)

Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A3. (b) : Hypophosphoric acid is $H_4P_2O_6$
oxidation state of P = +4.

A4. (a) : $P_4 + 20HNO_3(conc.) \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

A7. (b) : Ammonium nitrite ($NH_4Cl + NaNO_2$) gives N_2 on heating.

A8. (b) : $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

A9. (a) : NO_2 is a brown coloured gas.

A10. (b) : $2HNO_3 \xrightarrow{-H_2O} N_2O_5 + H_2O$

A11. (a) : $CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$

A12. (a) : NF_3 is least basic because electron pair on N is least available due to high electronegativity of F.

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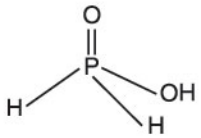
A13. (*d*) : $(NH_4)_2Cr_2O_7 \xrightarrow{Heat} Cr_2O_3 + N_2 + 4H_2O$

A16. (*b*) : No. of σ bonds = 16

B. *mcq from Competitive Examinations*

B1. (*b*) : Hypophosphorous acid is monoprotic acid.



B2. (*c*) : Reducing behaviour of H_3PO_2 is due to the presence of one —OH bond and two P—H bonds.

B3. (*b*) : NO_2 is not used as food preservative but SO_2 is used as a food preservative.

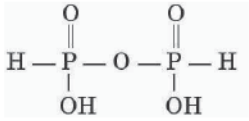
B4. (*a*) : Phosphinic acid (H_3PO_2) is monoprotic and phosphonic acid (H_3PO_3) is a diprotic acid.

B5. (*a*) : $CaC_2 + N_2 \longrightarrow CaCN_2 + C$

B6. (*c*) : $Cu + 4HNO_3$ (conc.) $\longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

B7. (*a*) : HNO_3 (+5), NO (+2), N_2 (0), NH_4Cl (–3)

B11. (*a*) : Pyrophosphorous acid ($H_4P_2O_5$) is a dibasic acid because it contains two P – O – H bonds :



B12. (*b*) : Cyclotrimetaphosphoric acid is $(HPO_3)_3$.
Oxidation state of P is
$+1 + x + 3(-2) = 0 \therefore x = +5$.

B13. (*e*) : Bismuth oxides are most basic. Oxides of N, P → acidic; oxides of As, Sb → amphoteric, oxides of Bi–basic.

B14. (*a*) : The P—H bond present in H_3PO_2 imparts reducing property to the acid.

$4\,AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3 + H_3PO_4$

B16. (*c*) : (*ii*) $H_2PO_4^-$ because it loses a proton and therefore, it is a Bronsted acid.

B17. (*a*) : The stability of hydrides decreases from NH_3 to BiH_3 due to increase in size of the central atom.

B18. (*a*) : $4Zn + 10HNO_3$ (dil.) $\longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

$Zn + 4HNO_3$ (conc.) $\longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

B19. (*a*) : Orthophosphorous acid: H_3PO_3
Oxidation state of P = +3
Pyrophosphorous acid : $H_4P_2O_5$
Oxidation state of P = +3

B20. (*d*) : $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$

B22. (*b*) : NO_2 is prepared by heating nitrates of heavy metals and not KNO_2.

$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$

$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$

$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$

$2KNO_3 \longrightarrow 2KNO_2 + O_2$

B23. (*e*) : Stability decreases down the group because size of central atom increases and its tendency to form covalent bond with small atom decreases.

B24. (*c*) : In group 15, catenation tendency of P is higher as compared to other elements of the group.

B25. (*a*) : In Ostwald's process, the formation of HNO_3 occurs as:

$4NH_3 + 5O_2 \xrightarrow[750-908\,^\circ C]{Pt} 4NO + 6H_2O + Energy$

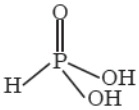
$2NO + O_2 \longrightarrow 2NO_2$

$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$

B28. (*d*) : $\underset{\text{Phosphorous acid}}{4H_3PO_3} \xrightarrow{\Delta} \underset{\text{Orthophosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3}$

B29. (*a*) : $P_4 + 3NaOH + 3H_2O \xrightarrow{CO_2} PH_3 + 3NaH_2PO_4$
PH_3 is less basic than NH_3.

B30. (*b*) : Basicity of H_3PO_3 is two because it has two ionizable H atoms



B31. (*c*) : In solid state, PCl_5 exists as $[PCl_4]^+\,[PCl_6]^-$

B32. (*a*) : $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

B33. (*d*) : Nitrogen has ability to form $p\pi$-$p\pi$ bonds with itself.

B34. (*a*) : $PBr_5 \rightleftharpoons [PBr_4]^+\,[Br^-]$

B36. (*a*) : $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4H_2O$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$2NH_4VO_3 \xrightarrow{\Delta} V_2O_5 + 2NH_3 + H_2O$

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

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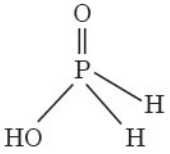
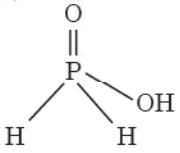
B37. (*d*) : $2NaN_3 \xrightarrow{\Delta} 3N_2 + 2Na$
Sodium azide

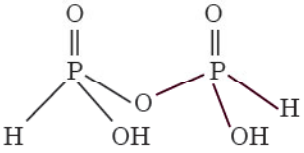
B38. (*c*) : H_3PO_2 is good reducing agent due to the presence of two P—H bonds.



B39. (*a*) :



(H_3PO_2)



$(H_4P_2O_5)$

B40. (*b*) : P_4 gives P_4O_6 when oxygen is in limited supply. Hence a mixture of O_2 and N_2 is most suitable.

$$P_4 + 3O_2 \xrightarrow{N_2} P_4O_6$$

B41. (*d*) : $Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba + 3N_2$.

B42. (*c*) :

$$P_4(s) + 3NaOH(aq) + 3H_2O \longrightarrow \underset{\text{Sodium hypophosphite}}{3\overset{+1}{N}aH_2\overset{}{P}O_2(aq)} + \underset{\text{Phosphine}}{\overset{-3}{P}H_3(g)}$$

$$3\overset{+1}{N}aH_2\overset{}{P}O_2(aq) \longrightarrow \overset{+5}{N}a_3\overset{}{P}O_4 + \overset{-3}{P}H_3$$

In the above reactions, phosphorus undergoes simultaneous oxidation and reduction to + 5 and – 3 oxidation states respectively. The reaction in which species undergoes oxidation and reduction are called disproportionation reactions.

B43. (*b*) : Nitric acid upon long standing turns yellow brown due to decomposition by sunlight into NO_2.

$$4HNO_3 \xrightarrow{\text{Sunlight}} 4NO_2 + 2H_2O + O_2$$

B44. (*d*) : The correct order is:

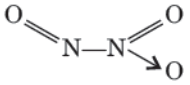
$$\overset{+5}{H_3}PO_4 > \overset{+4}{H_4}P_2O_6 > \overset{+3}{H_3}PO_3 > \overset{+1}{H_3}PO_2$$

C. mcq with more than one correct answer

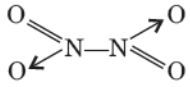
C1. (*b, c*) : P_4 has six PP bond and each ∠ PPP is 60°.

C3. (*a, b, c*) : N_2O $N{\equiv}N{\longrightarrow}O$

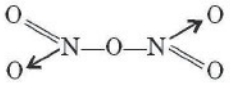
N_2O_3



N_2O_4



N_2O_5



C4. (*b, d*) : $P_4O_{10} + 4HNO_3 \longrightarrow 2N_2O_5 + 4HPO_3$

The nitrogen containing compound produced above is N_2O_5.

It cannot be prepared by the reaction of P_4 and HNO_3.

It is diamagnetic.

It does not contain N – N bond.

N_2O_5 is decomposed by alkali metals.

$N_2O_5 + Na \longrightarrow NaNO_3 + \underset{\text{Brown gas.}}{NO_2}$

C6. (*b, c*) : $NH_4NO_3 \longrightarrow N_2O + H_2O$

$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

$Ba(N_3)_2 \xrightarrow{\Delta} 3N_2 + Ba$

$Mg_3N_2 \xrightarrow{>700\,^\circ C} 3Mg + N_2$

Only $(NH_4)_2Cr_2O_7$ and $Ba(N_3)_2$ give N_2 on heating below 300 °C.

C7. (*a, b, c*) : Bi_2O_5 is more basic than N_2O_5

NF_3 is more covalent than BiF_3 because of lesser electronegativity difference.

Boiling point of NH_3 is more than PH_3 because of hydrogen bonding in NH_3.

P–P bond is stronger than N–N single bond because in N due to smaller size of atoms lone pair-lone pair repulsions will be more.

D. mcq based on passage/comprehension

D6. (*c*) : Nitrates being water soluble and as they get reduced by microbes so obviously its abundance will decrease.

D7. (*c*) : NH_3 is a stronger Lewis base than PH_3.

D8. (*b*) : $\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow 3NaH_2\overset{+1}{P}O_2 + \overset{+3}{P}H_3$

Here P_4 is oxidized to NaH_2PO_2 and it is reduced to PH_3

Matrix Match Type Questions

2. (*p, s*) : $3Cu + 8\underset{\text{(dil.)}}{HNO_3} \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO\uparrow$

(*q, s*) : $Cu + 4\underset{\text{(conc.)}}{HNO_3} \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2\uparrow$

(*r, t*) : $4Zn + 10\underset{\text{(dil.)}}{HNO_3} \longrightarrow 4\,Zn(NO_3)_2 + 5\,H_2O + N_2O\uparrow$

(*q, t*) : $Zn + 4\underset{\text{(conc.)}}{HNO_3} \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2\uparrow$

Competition File

Integer Type Questions

1. 2 : H_3PO_3 and $H_4P_2O_5$ are dibasic acids.

2. 2 : Phosphonic acid (H_3PO_3), pyrophosphoric acid ($H_4P_2O_5$) have oxidation state of +3 for phosphorus.

3. 5 : $PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$

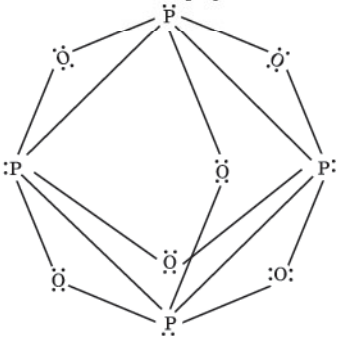
$PCl_5 + H_2O \longrightarrow POCl_3$

$PCl_5 + H_2SO_4 \longrightarrow POCl_3$

$6PCl_5 + P_4O_{10} \longrightarrow 10\ POCl_3$

$PCl_5 + O_2 \xrightarrow{\text{Heat}} POCl_3 + Cl_2$

4. 4 : In the structure of P_4O_6.

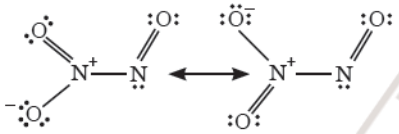


Number of lone pairs = 16

Number of P – O bonds = 12

Difference = 16 – 12 = 4

5. 8 :



It has 8 lone pairs of electrons.

NCERT Exemplar Problems : MCQs Type-I

2. (*c*) : Phosphorus involves $p\pi - d\pi$ bonds.

3. (*d*) : Because it has lowest bond dissociation enthalpy (E—H bond) and hence strongest reducing agent.

4. (*c*) : $4P + 3NaOH + 3H_2O \longrightarrow NaH_2PO_2 + PH_3$

PH_3 is less basic than NH_3.

5. (*c*) : Basicity of H_3PO_4 is three and it has three ionisable OH^-.

6. (*c*) : Strong reducing behaviour of H_3PO_2 is due to the presence of two P—H bonds.

7. (*b*) : $2Pb(NO_3)_2 \xrightarrow{\text{Heat}} 2PbO + 4NO_2 + O_2$

9. (*c*) : Maximum covalency of nitrogen is four.

10. (*a*) : Single P—P bond is stronger than N—N bond.

12. (*b*) : Only BiF_5 is known.

13. (*a*) : $(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} Cr_2O_3 + N_2 + 4H_2O$,

$Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba + 3N_2$

14. (*a*) : $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$

2 mol of NH_3 gives 2 mol of NO.

15. (*c*) : NaH_2PO_2 : Here $+1 + 2(+1) + x + 2(-2) = 0$

or $x = +1$

16. (*d*) : $2PCl_5 \rightleftharpoons [PCl_4]^+ \quad [PCl_6]^-$

tetrahedral (octahedral)

NCERT Exemplar Problems : MCQs Type-II

17. (*b*), (*d*) : It has six P—P bonds and four lone pairs of electrons.

❑❑❑

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Unit Practice Test

for Board Examination

Time Allowed: 1 hr. ***Maximum Marks: 25***

1. What is the covalence of nitrogen in N_2O_5? (1)

2. Give the disproportionation reaction of H_3PO_3. (1)

3. Give one reaction in which ammonia acts as a reducing agent. (1)

4. What happens when phosphorus is heated with concentrated NaOH is an inert atmosphere of CO_2? (1)

5. PCl_5 is known but PI_3 is not known. Why? (1)

6. Why does $R_3P{=}O$ exist but $R_3N{=}O$ does not exist (R = alkyl group)? Explain. (2)

7. Give the structures of P_4O_6 and P_4O_{10}. (2)

8. Explain.

(*i*) PCl_5 exists as $[PCl_4]^+ [PCl_6]^-$ but PBr_5 exists as $[PBr_4]^+ [Br]^-$.

(*ii*) NF_3 does not have donor properties like ammonia. (2)

9. Explain the following :

(*i*) NH_3 is a stronger base than PH_3.

(*ii*) Phosphorus (P_4) is more reactive than nitrogen (N_2).

(*iii*) H_3PO_3 is a diprotic acid. (3)

10. Explain the chemistry of manufacture of nitric acid by Ostwald's process? How does it react with iodine? (3)

11. Complete the following chemical quations:

(*i*) $Ca_3P_2\,(s) + H_2O\,(l) \longrightarrow$

(*ii*) $P_4O_{10} + H_2O \longrightarrow$

(*iii*) $Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow$ (3)

12. (*a*) Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

(*b*) Write the resonating structures of NO_2 and N_2O_5.

(*c*) Give two examples to show anomalous behaviour of nitrogen.

(*d*) Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15? Explain.

(*e*) Give the reaction of zinc with conc. HNO_3. (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part II of the book.

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UNIT 12

ORGANIC CHEMISTRY: BASIC PRINCIPLES AND TECHNIQUES

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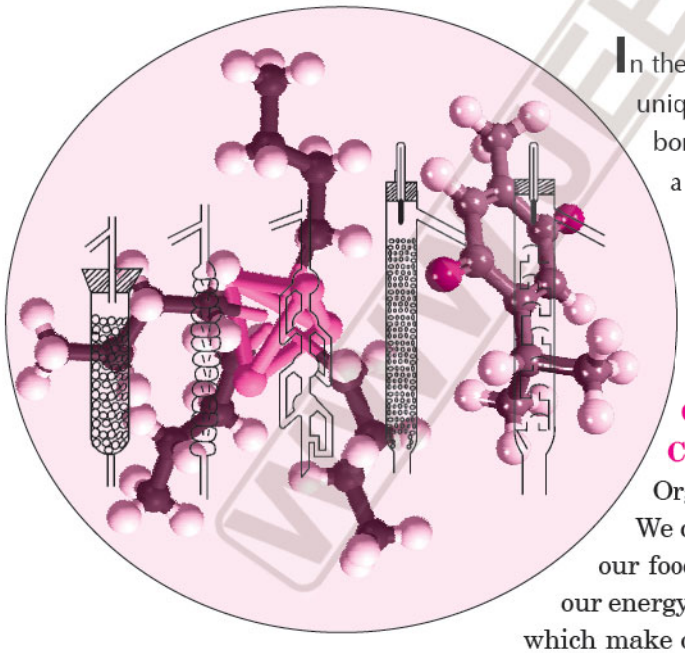

In the previous unit, we have studied that carbon atom has the unique property of **catenation** due to which it forms strong bonds with other carbon atoms to form chains and rings. It also forms strong bonds with other elements especially hydrogen, oxygen, nitrogen, sulphur, phosphorus and halogens, resulting millions of compounds. These compounds are studied under a separate branch of chemistry called **organic chemistry**.

GENERAL INTRODUCTION TO ORGANIC COMPOUNDS

Organic compounds are vital for sustaining life on earth. We depend on organic compounds that occur in nature for our food, for our clothing, for many of our medicines and for our energy (natural gas, petroleum, etc). These organic molecules which make our life possible include molecules like proteins which constitute essential compounds of our blood, muscles and skin, genetic information bearing deoxyribonucleic acid (DNA), enzymes, vitamins, lipids, carbohydrates, nucleic acids, etc. Our bodies are also regulated and defended by complex organic molecules. So, **organic chemistry plays a very vital role in our life**.

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VITAL FORCE THEORY

Until early nineteenth century, all the efforts of the chemists failed to synthesise organic compounds in the laboratory. It was believed that organic compounds cannot be prepared in the laboratory but can only be isolated from animals and plants. Berzelius, a Swedish chemist proposed that *the synthesis of these compounds within the plants and animals required some mysterious force*. This force was called vital force and the theory was referred to as **Vital force theory.**

However, the vital force theory received a crippling blow in 1828 when Friedrich Wohler, a German chemist accidently obtained **urea,** $(NH_2)_2CO$, an *organic compound* found in the urine of mammals. In fact, Wohler tried to prepare ammonium cyanate, a substance with mineral origin, by heating ammonium sulphate and potassium cyanate. But under the reaction conditions, ammonium cyanate rearranged to urea, a compound which was of organic nature.

$$\underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4} + \underset{\text{Potassium cyanate}}{2KCNO} \longrightarrow \underset{\text{Ammonium cyanate (Inorganic compound)}}{2NH_4CNO} + K_2SO_4$$

$$2NH_4CNO \xrightarrow{\text{Rearrangement | Heat}} \underset{\text{Urea (Organic compound)}}{2NH_2CONH_2}$$

This chance discovery of Wohler brought about a revolution in the field of organic chemistry. The synthesis of organic compounds no longer remained a mystery and many organic compounds were prepared in the laboratory. For example, *Kolbe* (1845) prepared acetic acid, *Hennel* (1828) prepared ethyl alcohol, *Berthelot* (1856) prepared methane etc. in the laboratory from mineral resources. Acetic acid was prepared from carbon and hydrogen as :

$$2C + H_2 \xrightarrow[\text{arc}]{\text{Electric}} \underset{\text{Acetylene}}{HC \equiv CH} \xrightarrow[HgSO_4]{\text{dil } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Acetic acid}}{CH_3COOH}$$

The synthesis of organic compounds altogether changed the very concept of organic chemistry. By the middle of nineteenth century, the Vital force theory was completely discarded. Chemists then never looked back and at present about ninety five per cent of the organic compounds are man-made.

Organic chemistry is now defined as the chemistry of carbon compounds as all organic compounds contain carbon as their essential constituent. Thus,

Organic chemistry *is the chemistry of compounds of carbon.*

The definition appears to be incomplete since there are many carbon compounds which are of inorganic nature. For example, carbon monoxide (CO), carbon dioxide (CO_2), carbon disulphide (CS_2), calcium carbonate ($CaCO_3$) etc., are all inorganic compounds although all of them contain carbon in them.

A detailed study of the structures of organic compounds shows that all of them contain carbon as their essential constituent and are also invariably associated with hydrogen. Consequently, organic compounds may be regarded as *hydrocarbons. i.e.,* compounds of carbon and hydrogen. A large number of organic compounds also contain elements like nitrogen, oxygen, sulphur, halogens, phosphorus, etc. which are derived from hydrocarbons by replacing one or more hydrogen atoms in their molecules with these atoms. Thus, the **modern definition** of the organic chemistry is **the chemistry of the hydrocarbons and their derivatives.**

TETRAVALENCY OF CARBON

The atomic number of carbon is 6 and its ground state electronic configuration is $1s^2 2s^2 2p_x^1\ 2p_y^1\ 2p_z^0$. Since it has four electrons in its outermost shell, its valency is four. To achieve noble gas configuration, carbon atom cannot lose or gain four electrons to form C^{4+} and C^{4-} ions because of the large amount of energy required for these processes (ionization enthalpy and electron gain enthalpy). Thus, it has a very little tendency to form

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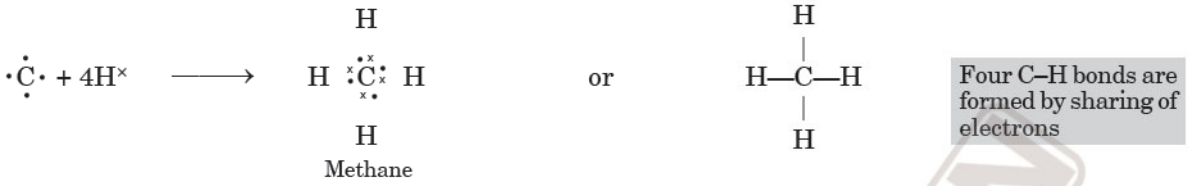
ionic compounds. Therefore, carbon achieves the noble gas configuration only by **sharing** electrons with other atoms and it forms **covalent bonds.**

Thus a carbon atom forms **four covalent bonds in its compounds.** For example, a molecule of methane (CH_4) is formed when four electrons of carbon are shared with four hydrogen atoms as shown below :

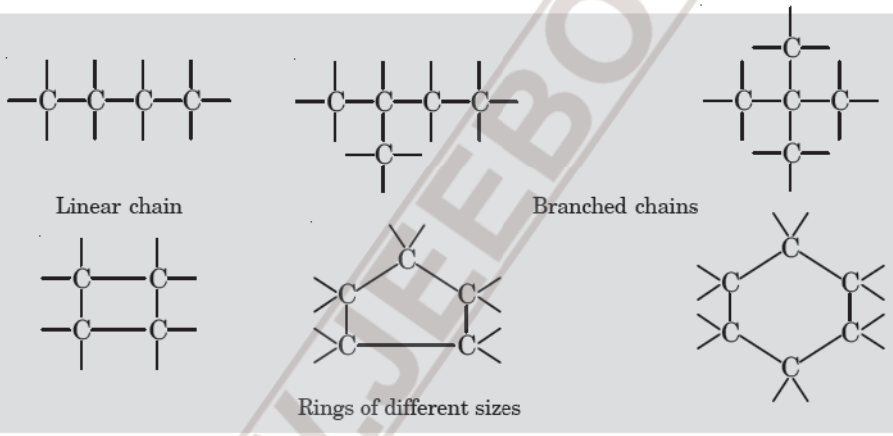


Methane

In a similar manner, carbon can complete its octet by sharing its valence electrons with the electrons of other atoms as well. *This tendency of carbon atom to form four covalent bonds is known as* **tetracovalency of carbon**.

Catenation : a unique property of carbon

Carbon atom has unique capacity to form bonds with other carbon atoms. **This property of forming bonds with atoms of the same element** is called **catenation**. Carbon shows maximum catenation in its group (group 14) in the periodic table. This is because of the larger bond strength of carbon to carbon bond as compared to that of other atoms. For example, C—C bond is very strong (335 kJ mol^{-1}) in comparison to Si—Si bond (220 kJ mol^{-1}) or Ge—Ge bond (167 kJ mol^{-1}). As a result, carbon atoms can link with each other to form either linear chains of various lengths or *branched chains* and even *rings* of different sizes as shown below :

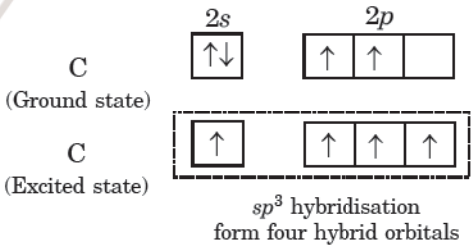


HYBRIDISATION AND SHAPES OF MOLECULES

We have studied in unit 4 that carbon atom forms four equivalent tetrahedral bonds because of **hybridisation** of its valence orbitals. This can explain the shapes of organic molecules. Let us recall the shapes of simple organic molecules on the basis of concept of hybridisation.

1. sp^3 Hybridisation and shapes of alkanes

The carbon atoms in alkanes involve sp^3 hybridisation. As a result, the four bonds formed by each carbon atom are directed towards the corners of a *regular tetrahedron.* For example, in case of methane (CH_4), the carbon atom involves sp^3 hybridisation and forms four sp^3 hybrid orbitals. Each of these forms sigma bond by



overlapping with 1*s*-orbitals of hydrogen. The four bonds are directed towards the corners of a regular tetrahedron as shown in Fig. 1 (*a*). The H–C–H bond angle in this molecule is 109°28' (or 109.5°). Thus, methane molecule has **tetrahedral** shape.

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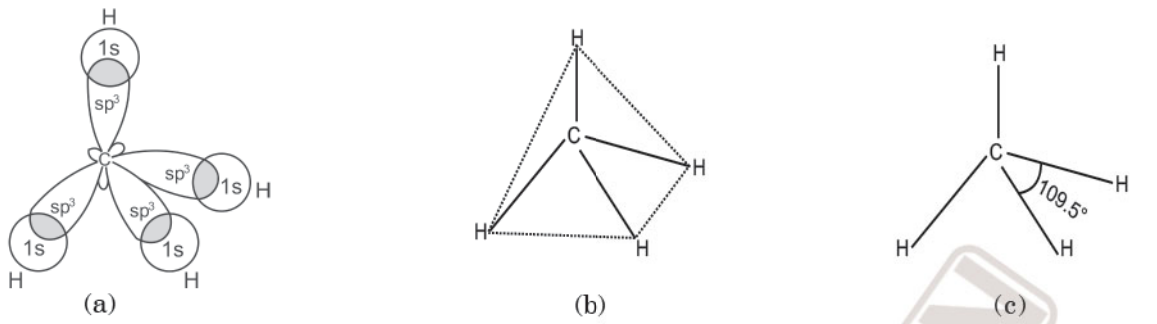


Fig. 1. Shape of methane.

The structure of methane molecule is also shown in Fig. 1 (*b*) and (*c*) .

In ethane ($H_3C–CH_3$) molecule, each carbon atom undergoes sp^3 hybridisation. One of the four sp^3 hybrid orbitals of one carbon atom overlaps axially with similar orbital of the other carbon atom to form C–C sigma bond. The remaining three hybrid orbitals belonging to both the carbon atoms overlap axially with the half-filled 1*s* orbitals of hydrogen atoms to form C–H sigma bonds as shown in Fig. 2.

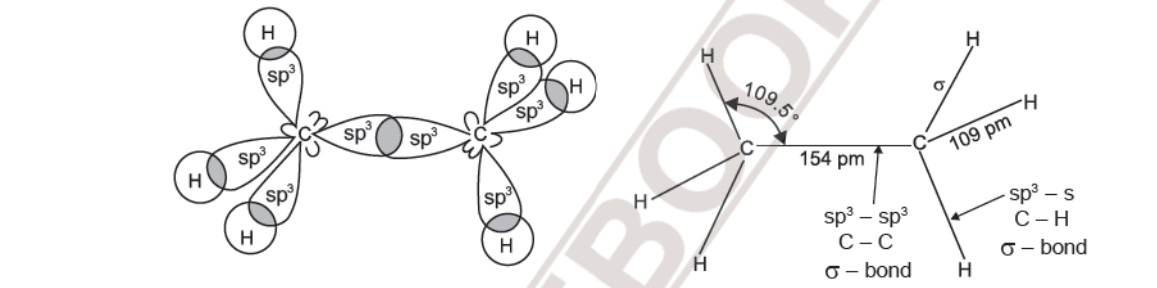
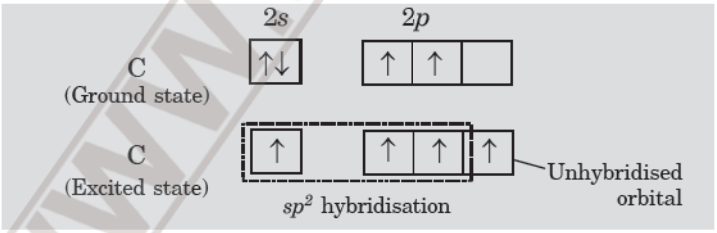


Fig. 2. Shape of ethane.

Thus, in ethane, C–C bond length is 154 pm and each C–H bond length is 109 pm.

2. sp^2 Hybridisation and shapes of alkenes

Alkenes are **planar** molecules and the carbon atoms of the C = C bond involve sp^2-hybridisation. Carbon atom has four unpaired electrons in the excited state. The three orbitals (one 2*s* and two 2*p*) get hybridised to form three sp^2-hybrid orbitals leaving one $2p_z$ unhybridised orbital.



For example in the case of ethylene one sp^2 hybrid orbital of one carbon atom overlaps with sp^2 hybrid orbital of the other carbon atom to form C—C sigma bond. The remaining two sp^2-hybrid orbitals of both the carbon atoms overlap with 1 *s*-orbitals of two hydrogen atoms to form C—H sigma bonds.

The unhybridised 2*p*-orbital (shown dotted) of one carbon atom overlaps with unhybridised 2*p*-orbital of other carbon atom to form pi (π) bond. The orbital structure of ethylene is shown in Fig. 3

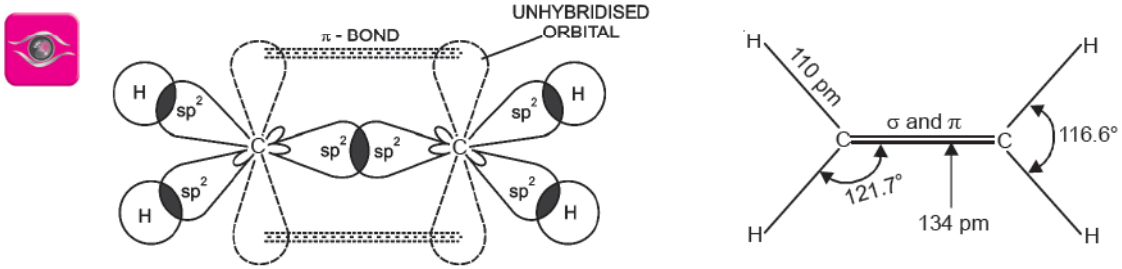


Fig. 3. Orbital structure of ethylene.

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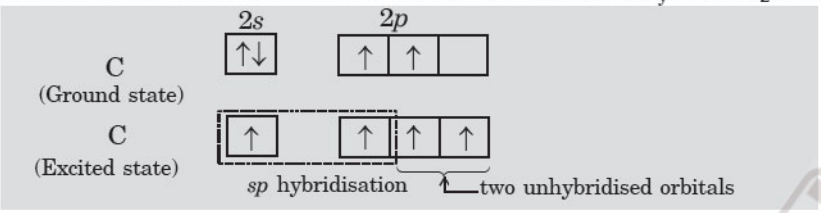
3. *sp* Hybridisation and shapes of alkynes

The two carbon atoms constituting the triple bond are *sp*-hybridised. In this, carbon undergoes *sp*-hybridisation forming two *sp*-hybrid orbitals. The two 2*p*-orbitals ($2p_y$ and $2p_z$) remain unhybridised.



For example, in the case of acetylene, one *sp*-hybrid orbital of one carbon atom overlaps with *sp*-hybrid orbital of the second carbon atom and forms C—C sigma bond. The remaining *sp*–hybrid orbital of each C-atom forms sigma bond with H-atom. Each of the unhybridised orbitals of one carbon atom forms π-bond with the second carbon atom so that there are two π-bonds in acetylene molecule. The structure of acetylene (ethyne) is shown in Fig. 4.

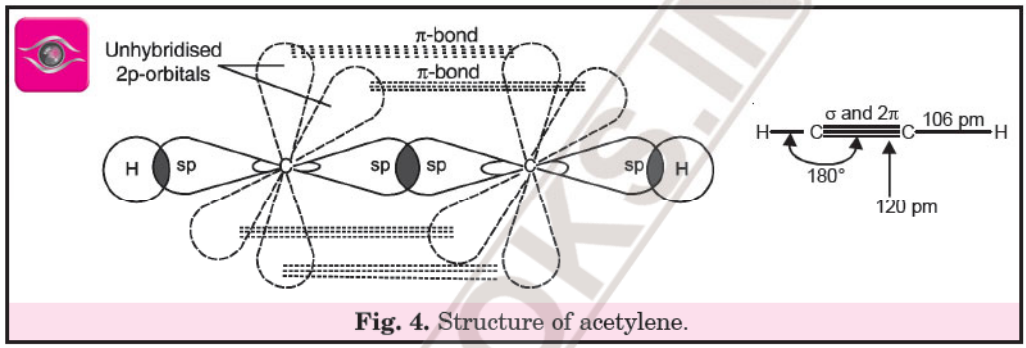


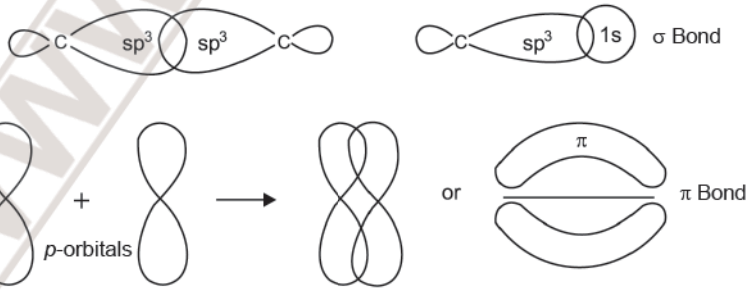
Fig. 4. Structure of acetylene.

Sigma and pi bonds

We have seen that ethylene molecule contains two bonds between carbon atoms, one is sigma(σ) bond and the other is pi (π) bond. Similarly, in acetylene, there is one sigma(σ) and two pi (π) bonds between carbon atoms. We have already learnt about these types of bonds in Unit 4.

Sigma (σ) bond is formed by the end to end overlapping of bonding orbitals along the internuclear axis. This overlapping is known as **head on overlap** or **axial overlap.** For example, the overlapping of sp^2 hybrid orbitals of two carbon atoms in ethylene or *sp* hybrid orbitals of two carbon atoms in acetylene.

Pi (π) bond is formed by the sidewise overlapping of the half filled atomic orbitals of bonding atoms. This overlap is known as **sidewise overlap** or **lateral overlap.** In this case, the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbital obtained as a result of sidewise overlap consists of two saucer type charged clouds above and below the plane of the participating atoms.



Sigma bonds are stronger bonds than π bonds because during the formation of σ bond, the overlapping of orbitals takes place to a larger extent.

Important features of π-bonds. As already discussed, the double bond in ethylene molecule consists of a σ-bond and a π-bond. The π-bond has some important features as given below :

1. In ethylene, as discussed earlier, the two 2*p* (unhybridised) orbitals participating in the π-bond are parallel to each other. For the proper sidewise overlap of these 2*p*-orbitals, all the atoms in C_2H_4 molecule must be in the same plane. Thus, the formation of π-bond restricts the molecule into a **planar shape.** Therefore, ethylene is a flat or planar molecule.

2. Due to the π-bond formed by sidewise overlap of 2*p*-orbitals, the rotation of one CH_2 fragment with respect to other will be hindered. The rotation of one carbon atom through 90° will break the π-bond because

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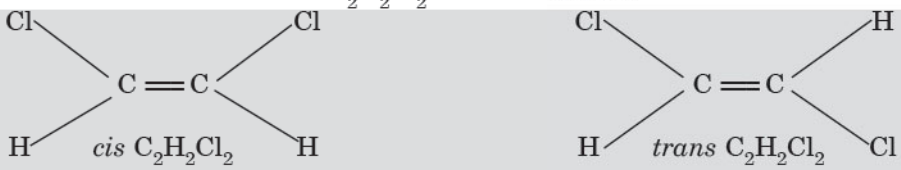
in that case, the unhybridised 2*p*-orbitals become perpendicular to each other and no sidewise overlap is possible. Hence, the rotation about the double bond is ***restricted* or *hindered.*** As a result, there are two distinct forms of molecules such as $C_2H_2Cl_2$ is shown below :



The first one is called the *cis* form (*cis*-1,2-dichloroethene) because the two Cl–atoms lie on the *same side* of the double bond. The other form is called *trans* (*trans*-1,2-dichloroethene) because the two Cl–atoms lie across the double bond from each other. Such type of molecules having same atom-to-atom bonding but different spatial arrangements are called *cis-trans* or *geometrical isomers.*

However, it may be noted that such type of isomerism is not possible in case of ethane (C_2H_6) because there is free rotation of one CH_3 fragment against another.

3. The electrons in the π-bonds are placed above and below the plane of the bonding atoms. These electrons are more exposed and therefore, are easily available to the electron seeking attacking reagents. Therefore, the π-bonded compounds are more reactive. In general, **π bonds provide the most reactive centres in the molcules containing multiple bonds.**

For example, ethene readily reacts with oxidising agents like potassium permanganate ($KMnO_4$) or potassium dichromate ($K_2Cr_2O_7$) at ordinary temperature. On the other hand, ethane (C_2H_6) (which has only σ electrons) is totally unaffected by these reagents at normal temperature. In general,

π-bonds provide the most reactive centres in unsaturated molecules.

SOLVED EXAMPLES

❑ Example 1.

How many sigma and pi bonds are present in each of the following molecules ?

(a) $CH_2 = C = CH_2$ *(b)* $CH_2 = CH - CH_2 - C \equiv CH$ *(c)* $CH_3C \equiv N$

Solution : *(a)* $CH_2 = C = CH_2$

$\sigma_{C-C} = 2, \sigma_{C-H} = 4$ — Total σ bonds = 6

$\pi_{C=C} = 2$ — Total π bonds = 2

(b) $CH_2 = CH - CH_2 - C \equiv CH$

$\sigma_{C-C} = 4, \sigma_{C-H} = 6$ — Total σ bonds = 10

$\pi_{C=C} = 3$ — Total π bonds = 3

(c) $CH_3C \equiv N$

$\sigma_{C-C} = 1, \sigma_{C-H} = 3\ \sigma_{C-N} = 1$ — Total σ bonds = 5

$\pi_{C=N} = 2$ — Total π bonds = 2

❑ Example 2.

What is the type of hybridisation of each carbon in the following compounds ?

(i) CH_3Cl *(ii)* $(CH_3)_2CO$ *(iii)* CH_3CN

(iv) $HCONH_2$ *(v)* $CH_3CH = CHCN$

N.C.E.R.T.

Solution : *(i)* $\overset{sp^3}{CH_3Cl}$: sp^3

(ii) $\overset{sp^3}{CH_3}-\overset{sp^2}{\underset{\underset{O}{\|}}{C}}-\overset{sp^3}{CH_3}$: sp^3, sp^2, sp^3

(iii) $\overset{sp^3}{CH_3}C\equiv\overset{sp}{N}$: sp^3, sp

(iv) $\overset{sp^2}{HC}(=O)NH_2$: sp^2

(v) $\overset{sp^3}{CH_3}\overset{sp^2}{CH} = \overset{sp^2}{CH}\,C \equiv \overset{sp}{N}$: sp^3, sp^2, sp^2, sp

❑ Example 3.

On the basis of type of hybridisation, predict the shape of the following molecules :

(i) $H_2C = O$ *(ii)* CH_3F *(iii)* $HC \equiv N$

N.C.E.R.T.

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Solution : (*i*) sp^2 hybridised carbon and therefore, shape is **trigonal planar.**
(*ii*) sp^3 hybridised carbon and shape is **tetrahedral.**
(*iii*) *sp* hybridised carbon and shape is **linear.**

Practice Problems

1. How many σ and π bonds are present in each of the following molecules ?
(*i*) $HC \equiv C - CH = CHCH_3$ (*ii*) C_6H_{12}
(*iii*) $CH_2 = C = CHCH_3$ (*iv*) $CH_2 = C = CH - CH = CH_2$ **N.C.E.R.T.**

2. What is the type of hybridisation of each carbon in the following compounds ?
(*i*) CH_3CH_3 (*ii*) CH_3Cl
(*iii*) $(CH_3)_2CO$ (*iv*) $CH_2 = CN$

3. Give hybridisation state of each carbon atom in the following molecules :
(*i*) $CH_3 - CH = CH_2$ (*ii*) $CH_2 = C = O$
(*iii*) $CH_2 = CHCN$ (*iv*) $HCONH_2$

4. Write the state of hybridisation of all the carbon atoms in $CH_2 = C = CH_2$.

5. Give hybridisation state of each carbon in following compounds :
(*i*) $CH_2 = C = O$ (*ii*) $CH_3 - CH = CH_2$ (*iii*) $(CH_3)_2CO$ (*iv*) $CH_2 = CHCN$
(*v*) $CH_3\overset{-}{C}H_2$ (*vi*) $CH_3\overset{+}{C}H_2$ (*vii*) CH_3CH_3

6. Indicate the σ and π bonds in the following molecules :
(*i*) C_2H_6 (*ii*) C_6H_{12} (*iii*) CH_2Cl_2
(*iv*) $CH_2 = C = CH_2$ (*v*) CH_3NO_2 (*vi*) $HCONHCH_3$

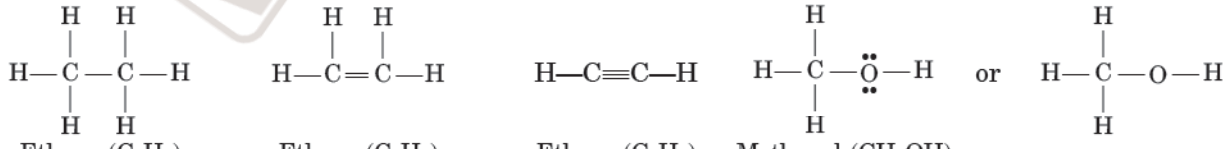
Answers to Practice Problems

1. (*i*) 10, 3 (*ii*) 17, 1 (*iii*) 9, 2 (*iv*) 10, 3
2. (*i*) sp^3, sp^3 (*ii*) sp^3 (*iii*) sp^3, sp^2 (*iv*) sp^2, *sp*
3. (*i*) sp^3, sp^2, sp^2 (*ii*) sp^2, *sp* (*iii*) sp^2, sp^2, *sp* (*iv*) sp^2
4. Carbon 1 and 3 are sp^2 hybridised and carbon 2 is *sp* hybridised.
5. (*i*) sp^2, sp (*ii*) sp^3, sp^2 sp^2 (*iii*) sp^3 sp^2, sp^3 (*iv*) sp^2, sp^2, *sp* (*v*) sp^3 sp^3 (*vi*) sp^3 sp^2 (*vii*) sp^3 sp^3
6. (*i*) 7σ (*ii*) 17σ, 1π (*iii*) 4σ (*iv*) 6σ, 2π (*v*) 6σ, 2π (*vi*) 8σ, 1π

STRUCTURAL REPRESENTATION OF ORGANIC COMPOUNDS

Structural Formulae

The atomic composition of a molecule is represented by a molecular formula. The molecular formula gives the number and types of various atoms present in a molecule. The structures of organic compounds are represented in several ways. The ***Lewis structure*** is the simplest method of representing any molecule by showing the involvement of electrons between bonds. However, the Lewis structures can be simplified by representing the two electron covalent bonds by a dash (—). In this representation, a single bond is represented by a single dash (—), a double bond by a double dash (=) and a triple bond by a triple dash (≡). The lone pairs of electrons on heteroatoms (*e.g.*, oxygen, nitrogen, sulphur, halogens, etc.) may or may not be shown. This representation is called **structural formula.** For example, the structural formulae of ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol (CH_3OH) may be shown as below :



Condensed Formulae

The structural formulae as shown above are time consuming. These may be simplified in a **condensed formula.** In this formula, the arrangement of atoms are shown but the bonds (dashes) between (some or all) may be omitted and the number of identical groups attached to an atom are indicated by a subscript. For example,

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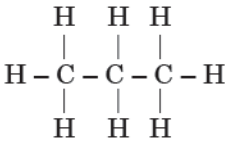

may be represented as $CH_3–CH_2–CH_3$ or $CH_3CH_2CH_3$

Similarly, ethane, ethene, ethyne and methanol may be written as

CH_3CH_3	$H_2C = CH_2$	$HC \equiv CH$	CH_3OH
or C_2H_6	or C_2H_4	or C_2H_2	Methanol
Ethane	Ethene	Ethyne	

The long condensed formulae may be further simplified wherever possible. For example, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$ can be condensed to $CH_3(CH_2)_6COOH$.

Bond-line Structural Formulae

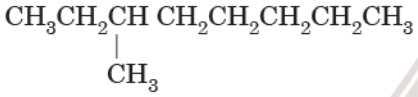
To further simply the formulae, the organic chemists use another way of representation known as ***bond line structural representation.*** In this representation, the carbon and hydrogen atoms are not shown and the lines between carbon–carbon bonds are shown in a zig-zag manner. For example, hexane has a continuous chain of six carbon atoms which may be represented as :

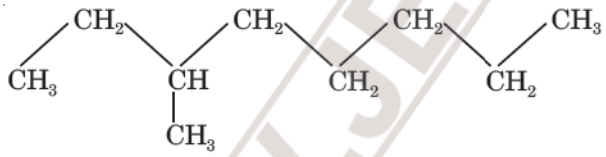
$CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$

Hexane

The atoms other than carbon and hydrogen are written. **The terminals denote methyl ($–CH_3$) groups unless indicated otherwise by a functional group while the line junctions denote carbon bonded to appropriate number of hydrogen atoms required to satisfy the valency of the carbon atoms.** For example the molecule, octanoic acid, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$ may be represented in bond line formula as :

Similarly, 3-methyloctane may be represented by the following forms as :

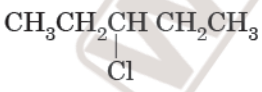
(*i*) 

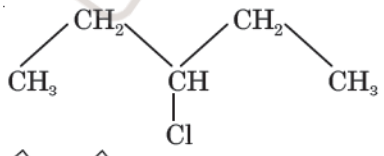
(*ii*) 

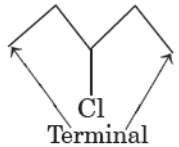
(*iii*)

Terminals represent methyl groups

Similarly, 3-chloropentane may be represented as

(*i*) 

(*ii*) 

(*iii*) 

Terminal methyl groups

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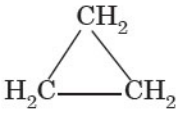
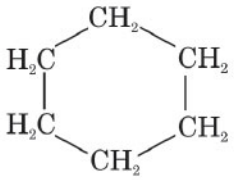
Cyclic Compounds or Polygon Formulae

There are many organic compounds in which carbon atoms are joined by rings. These compounds containing one or more rings are called **cyclic compounds.** These are represented by drawing the appropriate ring (polygon) without showing the carbon and hydrogen atoms. In this representation, the corner of the ring (polygon) represents a carbon atom and the sides of the polygon denote a carbon–carbon bond. The atom or group of atoms other than hydrogen are shown in the structure. For example,



Cyclopropane

is represented as



Cyclohexane

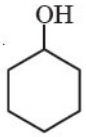
is represented as

Some other examples of cyclic compounds are :

Cyclobutane

Cyclopentane

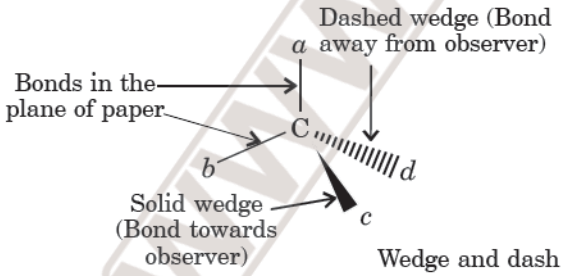
Chlorocyclohexane

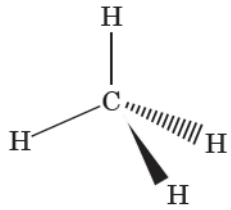


Cyclohexanol

Three Dimensional Representation of Organic Molecules

The three dimensional (3–D) structure of organic molecules is very difficult to draw on a paper (two dimensional). Therefore, certain graphic conventions have been proposed. The simplest convention is *solid* and *dashed wedge formula,* in which 3–D image of a molecule can be preceived from two dimensional picture. In this representation, a tetrahedral molecule with four atoms or groups *a, b, c* and *d* bonded to it can be represented by a **wedge formula**. A solid wedge (◄) (or a heavy line) is used to indicate a bond projecting above the plane of the paper (*i.e.* bond projecting towards you) and the dashed wedge (▪▪▪▪▪▪▪▪) (or a dashed line) is used to depict the bond below the plane (*i.e.,* bond pointing away from you). The bonds lying in the plane of the paper are shown by normal lines. For example, in the tetrahedral molecule C*abcd*, the two bonds C–*a* and C–*b* are shown by the normal lines and are in the plane of the paper, the C –*c* bond connected by solid wedge is intended to be in front of the plane while C – *d* bond connected by dashed line is behind this plane. The wedge and dash representation of CH_4 molecule is also shown below :





Wedge and dash representation

Projection Formulae

In organic molecules, the three dimensional arrangement of atoms in space can be represented in plane by *projection formulae.* These formulae are obtained by actually projecting the 3–D model of a molecule using a ray of light. The two dimensional image of the molecule is drawn on the paper according to certain conventions. The projection of the molecule can be obtained by orientating the molecule in different ways with respect to the plane of the paper. There are three different types of projection formulae. These are *Fischer projection, Newmann projection* and *Sawhorse projection formulae*. These are discussed in the next chapters.

Molecular Models

To have better visualisation and perception of three dimensional shapes of organic molecules, the molecular models are used. These are made of wood, plastic or metals and are commercially available. Generally, three types of molecular models are used. These are:

(*i*) *Framework model* (*ii*) *Ball and stick model* and (*iii*) *Space filling model.*

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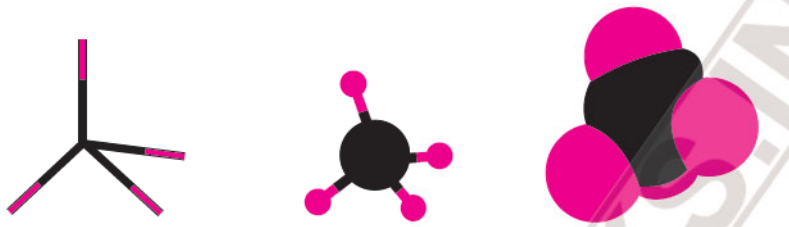
(*i*) In the **framework model**, only the bonds connecting the atoms of a molecule are shown. In this model, atoms are not shown. This model gives the pattern of bonds of a molecule.

(*ii*) In the **ball and stick model,** both the atoms and the bonds are shown. In this model, balls represent atoms and sticks represent bonds. The unsaturated compounds containing double bonds or triple bonds (C = C or C ≡ C) are represented by using springs in place of sticks.

(iii) In the ***space filling model,*** emphasis is given on the relative size of each atom. In this model, bonds are not shown. This model also tells the volume occupied by each atom in the molecule.

In addition to these models computer graphics are also used these days for molecular modeling.

These three types of models are shown for methane molecule in Fig. 5.



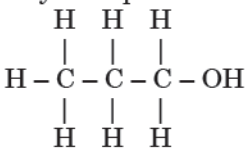
(*i*) Framework model (*ii*) Ball and stick model (*iii*) Space filling model

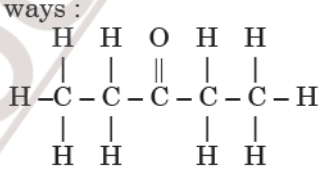
Fig. 5. Different molecular models for methane (CH_4).

Sum up

The organic molecules may be represented in the following ways :

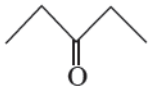
Structural formula



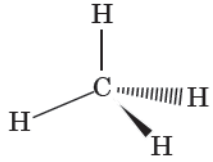


Condensed formula $CH_3CH_2CH_2OH$ $CH_3CH_2COCH_2CH_3$

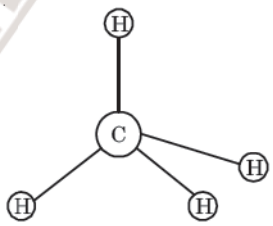
Bond line structural formula



Three dimensional formula



Wedge and dash representation



Molecular model (Ball and stick model)

SOLVED EXAMPLES

❑ **Example 4 .**

For each of the following compounds write the condensed formula and bond line formula :

(i) $CH_3CH_2CH_2CH_2CH_2CH_2\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-\overset{\displaystyle H}{\overset{|}{C}}=O$

(ii) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(iii) $N\equiv C-\underset{\displaystyle OH}{\underset{|}{CH}}-C\equiv N$

(iv) $HO\,CH_2\,CH_2\,CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}\,\overset{\displaystyle CH_3}{\overset{|}{CH}}\,CH_3$

(v) $NH_2-CH_2\,CH_2\,CH_2\,CH_2\,CH_2\,CH_2\,COOH$

N.C.E.R.T.

Solution : Condensed formula :

(i) $CH_3\,(CH_2)_5CHBrCH_2CHO$ *(ii)* $(CH_3)_2\,CHCH_2OH$ *(iii)* $(CN)_2CHOH$

(iv) $HO(CH_2)_3CH(CH_3)CH(CH_3)_2$ *(v)* $H_2N-(CH_2)_6-COOH$

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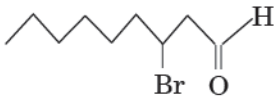
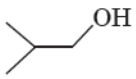
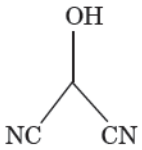
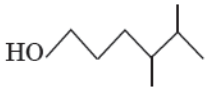
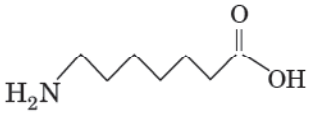
Bond line formula :

(i) 

(ii) 

(iii) 

(iv) 

(v) 

❑ Example 5.

Expand each of the following condensed formulae into their complete structural formulae :

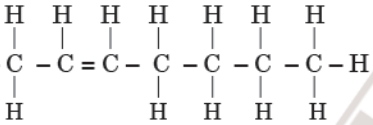
(a) $CH_3CH = CH(CH_2)_3CH_3$

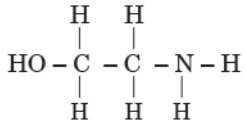
(b) $HOCH_2CH_2NH_2$

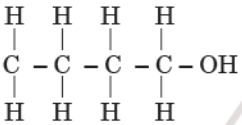
(c) $CH_3(CH_2)_2CH_2OH$

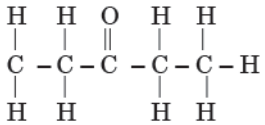
(d) $CH_3CH_2COCH_2CH_3$

Solution :

(a) 

(b) 

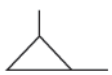
(c) 

(d) 

❑ Example 6.

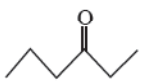
Draw all polygon formulae for the molecular formula C_5H_{10}.

Solution : The different polygon formulae of the compound having molecular formula C_5H_{10} are :

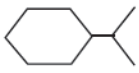
(i) (ii) (iii) (iv) (v) 

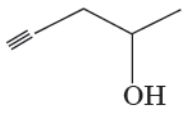
❑ Example 7.

Expand each of the following bond line formulae to show all the atoms including carbon and hydrogen.

(i) 

(ii)

(iii) 

(iv) 

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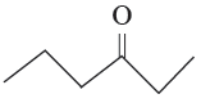
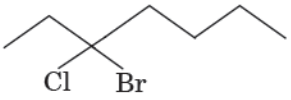
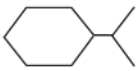
(v)

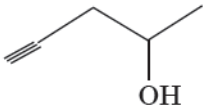
(vi)

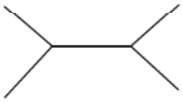
Solution :

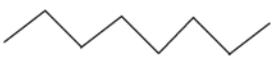
(i) 

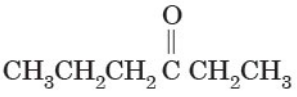
(ii) 

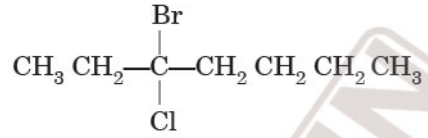
(iii) 

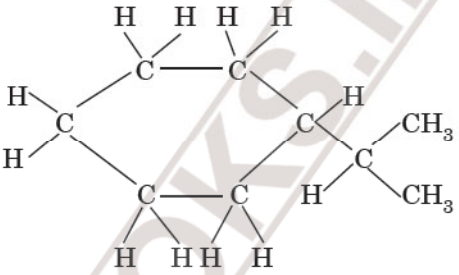
(iv) 

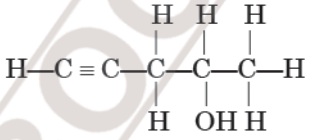
(v) 

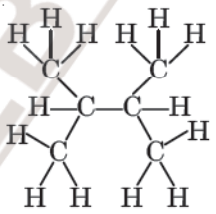
(vi) 

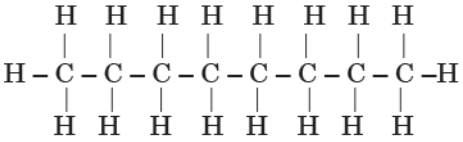










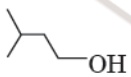


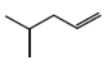
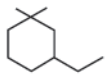
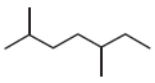
Practice Problems

7. Rewrite each of the following condensed structural formulae, as dash structural (or dash) formulae and as bond line formulae :

(i) $(CH_3)_3\ C\ CH_2CH_3$ *(ii)* $CH_3\ \underset{\underset{O}{\|}}{C}\ CH_2CH(CH_3)_2$ *(iii)* $CH_3CH(OH)CH_2CH_2OH$

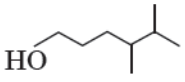
8. Write structural formulae for each of the following bond line formulae :

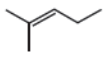
(i) 

(ii)  *(iii)*  *(iv)* 

9. Write bond line formulae for the following :

(i) $HO\ (CH_2)_3\ CH\ CH_3\ CH\ (CH_3)_2$ *(ii)* $CH_3\ \underset{\underset{CH_3}{|}}{C} = CH\ CH_2\ CH_3$

Ans. *(i)* 

(ii) 

10. Write three dimensional (wedge-dashed wedge–line) representation for the following :

(i) CH_3Cl *(ii)* CH_3CH_2OH

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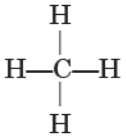
CLASSIFICATION OF ORGANIC COMPOUNDS

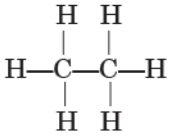
The simplest organic compounds containing only carbon and hydrogen are calld ***hydrocarbons***. These are regarded as the parent organic compounds and all other compounds are considered to be derived from them by the replacement of one or more hydrogen atoms by other atoms or groups of atoms. They have been broadly classified as :

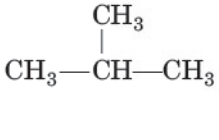
1. *Open chain or acyclic compounds.*
2. *Closed chain or cylic or ring compounds.*

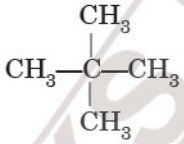
1. Open chain or acyclic compounds

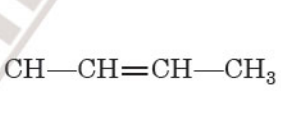
These compounds contain open chains of carbon atoms in their molecules. The carbon chains may be either straight chains or branched chains. They are called **aliphatic compounds** because the earlier compounds of this class were obtained either from animal or vegetable fats (Greek *aliphatos* meaning fats).

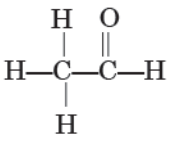

Methane

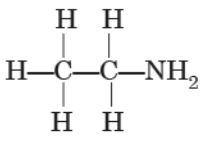

Ethane

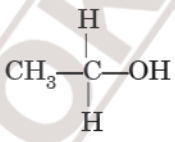

Isobutane

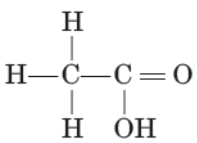

Neopentane


But-2-ene


Acetaldehyde


Ethyl amine

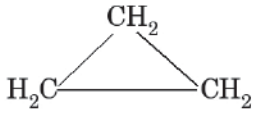

Ethyl alcohol

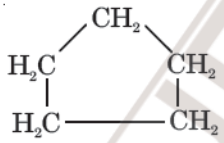

Acetic acid

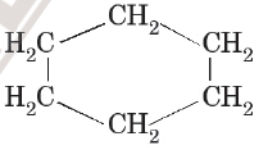
2. Closed chain or cyclic or ring compounds.

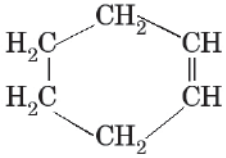
These compounds contain closed chains or rings of atoms in their molecules. These compounds may be ***carbocyclic*** (containing rings of carbon atoms only) or ***heterocyclic*** (containing rings of carbon atoms or one or more heteroatoms). The cyclic compounds are of three types :

(*i*) Alicyclic compounds . *These compounds contain a ring of three or more carbon atoms in them.* They resemble aliphatic compounds in many of their properties. For example,

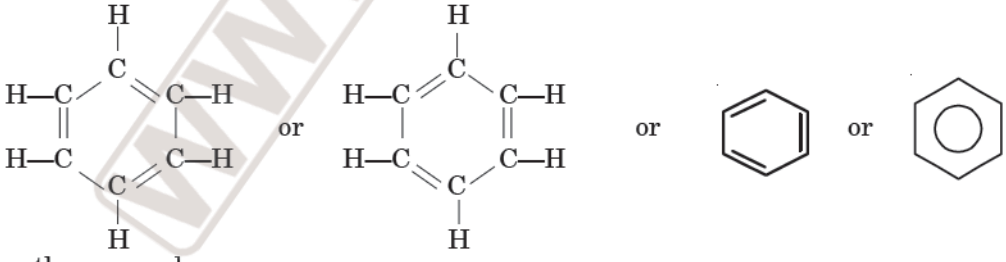

Cyclopropane


Cyclopentane

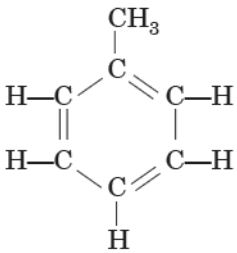

Cyclohexane

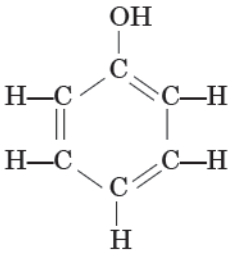

Cyclohexene

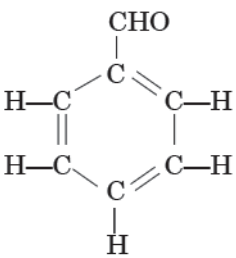
(*ii*) Aromatic compounds. *These have a cyclic system containing at least one benzene ring.* The parent member of the family is called benzene. Benzene has a homocyclic hexagonal ring of six carbon atoms with three double bonds in the alternate positions. Benzene can be represented by any of the following structures :

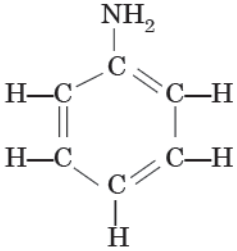


Some other examples are :


Toluene


Phenol


Benzaldehyde


Aniline

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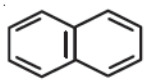
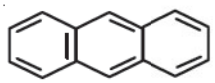
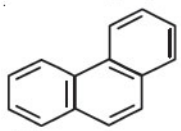
These compounds are also called **benzenoid compounds** and they exhibit special property known as **aromaticity** (discussed later). Bicyclic and tricyclic compounds also belong to this category.



Naphthalene
(Bicyclic)



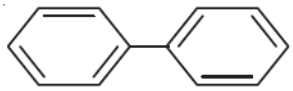
Anthracene
(Tricyclic)



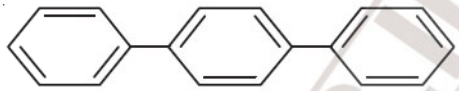
Phenanthrene
(Tricyclic)

Compounds containing two or more benzene rings fused together are called **polycyclic aromatic** compounds.

Besides, compounds containing fused benzene rings, benzenoid compounds may contain isolated benzene rings. For example,

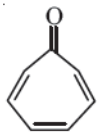


Biphenyl or diphenyl

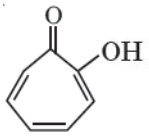


Terphenyl

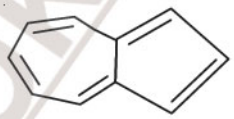
In addition to these, there are some compounds which show aromaticity but donot contain any benzene ring. These are called **non-benzenoids.** For example,



Tropone

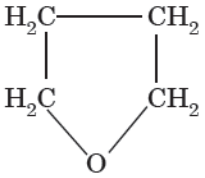


Tropolone

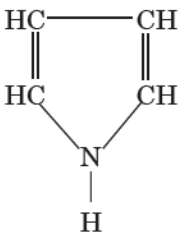


Azulene

***(iii)* Heterocyclic compounds.** *In these compounds, the ring contains one or more atoms of either nitrogen, oxygen or sulphur in addition to carbon atoms.* The atom other than carbon (such as N, O, S) present in the ring is called *hetero atom.* Some common examples are :

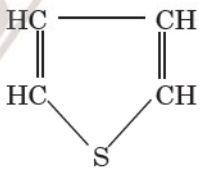


Tetrahydrofuran
(THF)

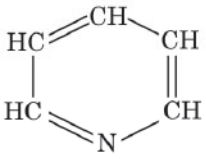


Pyrrole

Furan

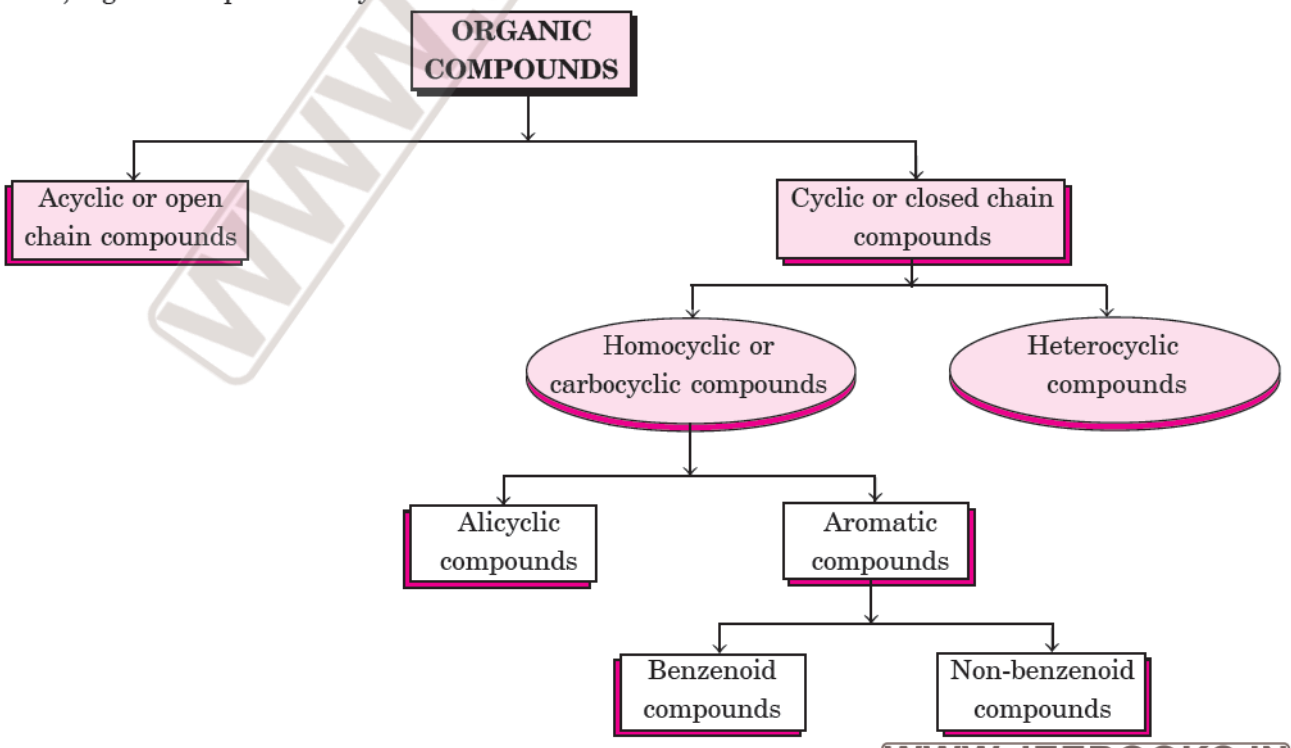


Thiophene



Pyridine

Thus, organic compounds may be classified as :



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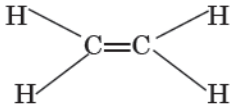
FUNCTIONAL GROUP

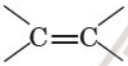
The organic compounds except alkanes contain some **structural features** which make it possible to classify compounds by reactivity. These are called **functional groups.** These functional groups are responsible for the characteristic properties of the compounds. A functional group is a group of atoms within a molecule that has a characteristic chemical behaviour. Thus, **functional group** may be defined as

an atom or group of atoms that determines the characteristic chemical properties of an organic compound.

For example, one of the simplest functional groups is the carbon–carbon double bond. It makes a special class of organic compounds called **alkenes.**

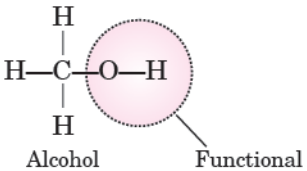


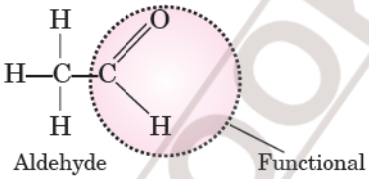
Ethene

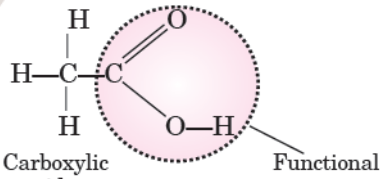
Functional group : 

In some cases, the carbon bonded to some other atoms such as N, O, S, P, etc. acts as a functional group.

For example, the family of **alcohols** have its characteristic properties due to the presence of —OH (hydroxy) group, called functional group. Similarly, **aldehydes** owe their characteristic properties to the functional group —CHO (aldehydic), **carboxylic acids** have properties due to —COOH (carboxylic acid) group and so on.



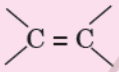
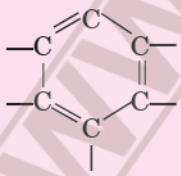




Some Important Functional Groups and Families

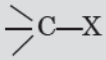
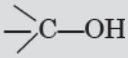
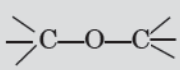
1. Functional groups containing carbon-carbon multiple bonds

Some compounds containing carbon–carbon multiple bonds give characteristic reactions and constitute **different families.** These are :

Family	Characteristic structural feature or group	
Alkenes		Carbon-carbon double bond
Alkynes		Carbon-carbon triple bond
Arenes		Alternate single and double bonds in a six membered ring of carbon atoms. The ring is also called **aromatic ring.**

2. Functional groups with carbon bonded to other atoms like O, N, S or P.

Some compounds contain functional groups containing carbon bonded to other atoms like O, N, S or P. These are bonded by single bonds as well as by double bonds. For example, the common families containing carbon bonded to other atoms by single bonds are :

Compound	Structure	Functional group
Alkyl halide		–X
Alcohols		– OH
Ethers		– O –

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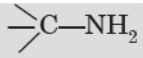
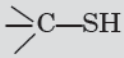
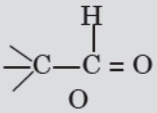
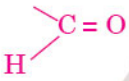
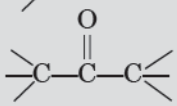
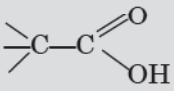
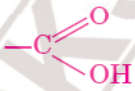
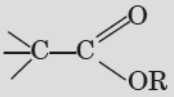
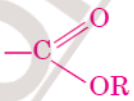
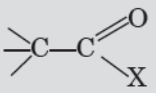
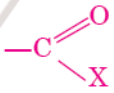
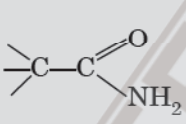
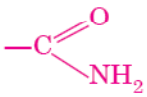
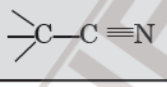
Amines		$-NH_2$
Thiols		–SH

In amines carbon is bonded to N and in thiol carbon is bonded to sulphur.

The families containing carbon bonded to oxygen by double bond are :

Compound	Structure	Functional group
Aldehydes		
Ketones		
Carboxylic acids		
Esters		
Acid halides		
Amides		
Nitrile		

'R' stands for alkyl groups such as CH_3-, C_2H_5-, C_3H_7-, etc.

* In nitriles, carbon is bonded to N by a triple bond.

HOMOLOGOUS SERIES

The organic compounds have been classified into various families. Each family contains closely related organic compounds so far as their structures and chemical properties are concerned. The different families or classes are known as homologous series. **A homologous series** may thus, be defined as

a series of similarly constituted compounds in which the members possess the same functional group and have similar chemical characteristics.

The two consecutive members differ in their molecular formula by —CH_2 group.

The different members of a series are known as **homologues**. A few members of the alcohol family are given below :

Formula	Name
CH_3OH	Methyl alcohol
C_2H_5OH	Ethyl alcohol
C_3H_7OH	Propyl alcohol
C_4H_9OH	Butyl alcohol

Characteristics of homologous series. The common characteristics of the members present in a homologous series are :

(*i*) All the members of a series can be represented by the general formula. For example, the members of the alcohol family are represented by the formula $C_nH_{2n+1}OH$ where n may have values 1, 2, 3.....etc.

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(*ii*) Two successive members differ in their formula by —CH_2 group or by 14 atomic mass units (12 + 2 × 1).

(*iii*) Different members in a family have common functional group *e.g.,* the members of the alcohol family have —OH group as the functional group.

(*iv*) The members in any particular family have almost identical chemical properties and their physical properties such as melting point, boiling point, density, solubility etc., show a proper gradation with the increase in the molecular mass.

(*v*) The members present in a particular series can be prepared almost by similar methods known as the *general methods of preparation*.

DIFFERENT CLASSES OF ALIPHATIC COMPOUNDS AND THEIR NOMENCLATURE

Nomenclature implies assigning proper name to a particular organic compound on the basis of certain standard rules so that the study of these compounds may become systematic. In case of aliphatic compounds, two systems of naming are generally used :

(A) *Trivial system* (B) *IUPAC system*.

(A) Trivial system.

In earlier days, the organic compounds were named after the source from which they were obtained. For example, urea got its name because the compound was obtained from the urine of the mammals. Similarly, methyl alcohol was called *wood spirit* since it could be obtained as one of the products during the destructive distillation of wood; *formic acid* derived its name from the Greek word *formicus* (red ants) since the acid could be obtained from red ants. These names are without any systematic basis and are known as **common names** or **trivial names**. Such a system of nomenclature is known as **trivial system**.

The common names of some popular organic compounds are given in Table 1.

Table 1. Common or trivial names of some organic compounds.

Compound	Common name	Compound	Common name
CH_4	Methane	$(CH_3CH_2)_2O$	Diethyl ether
C_2H_4	Ethylene	$CHCl_3$	Chloroform
C_2H_2	Acetylene	CHI_3	Iodoform
$H_3CCH_2CH_2CH_3$	*n*-Butane	CH_3CN	Acetonitrile
$(H_3C)_2CHCH_3$	Isobutane	CH_3COOH	Acetic acid
$(H_3C)_4C$	Neopentane	$CH_3OCH_2CH_3$	Ethyl methyl ether
HCHO	Formaldehyde	C_6H_6	Benzene
CH_3CHO	Acetaldehyde	$C_6H_5CH_3$	Toluene
$(H_3C)_2CO$	Acetone	$C_6H_5NH_2$	Aniline
CH_3CH_2OH	Ethyl alcohol	C_6H_5OH	Phenol
$CH_3CH_2CH_2OH$	n-Propyl alcohol	$C_6H_5OCH_3$	Anisole
CH_3CONH_2	Acetamide	$C_6H_5COCH_3$	Acetophenone
CH_3OCH_3	Dimethyl ether	$C_6H_5CONH_2$	Benzamide

(B) IUPAC system.

In order to rationalise the system of naming, an *International Congress of Chemists* was held in Geneva in 1892. They adopted certain uniform rules for naming the compounds.

The system of nomenclature was named as **Geneva system.** Since then the system of naming has been improved from time to time by the *International Union of Pure and Applied Chemistry* and the new system is called **IUPAC system** of naming. This system of nomenclature was first introduced in 1947 and was modified from time to time. The most exhaustic rules for nomenclature were first published in 1979 and later revised and updated in 1993. The rules discussed in the present chapter are based on guide books published by IUPAC in 1979 (**Nomenclature of Organic Chemistry** by J. Rigandy and S.P. Klesney) and 1993 (**A Guide to IUPAC Nomenclature for Organic Chemistry** by R. Panico, W.H. Powell and J.C. Richer). With the help of this system, an organic compound having any number of carbon atoms can be easily named.

Though most of the books discuss nomenclature based on the IUPAC recommendations of 1979, we include here the recommendations of 1993 also to provide LATEST UPDATED RULES.

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IUPAC System of Naming Organic Compounds

In the IUPAC system, the name of an organic compound consists of three parts :

(*i*) *Word root* (*ii*) *Suffix* (*iii*) *Prefix.*

(*i*) Word root. *The word root denotes the number of carbon atoms present in the chain.* For chains containing upto four carbon atoms, special word roots (*meth*—C_1, *eth*—C_2, *prop*—C_3 and *but* —C_4) have been used while for those containing more than four carbon atoms, Greek numerals have been used to represent the word root. For example,

Chain length	Word root	Chain length	Word root
C_1	Meth	C_8	Oct
C_2	Eth	C_9	Non
C_3	Prop	C_{10}	Dec
C_4	But	C_{11}	Undec
C_5	Pent	C_{12}	Dodec
C_6	Hex	C_{20}	Icosane
C_7	Hept	C_{30}	Triacontane

(*ii*) Suffix. The word root is linked to the suffix which may be *primary* or *secondary* or *both*.

(*a*) Primary suffix. *It indicates the nature of linkages in the carbon atoms*. For example, if the carbon atoms are linked by single covalent bonds (C—C), the primary suffix ***-ane*** is used. Similarly, for a double bond (C = C) between the carbon atoms, the suffix is ***-ene*** while for the triple bonded carbon atoms (C ≡ C), suffix ***-yne*** is used. Thus the suffixes are :

ane — for single bonded compounds, C—C
ene — for double bonded compounds, C = C
yne — for triple bonded compounds, C ≡ C

If the parent chain contains two, three or more double or triple bonds, then the numerical prefixes such as **di** (for two), **tri** (for three), **tetra** (for four), etc. are added to the primary suffix.

It may be noted that **extra 'a'** is added to the word root if the primary suffix to be added begins with a consonant (other than *a, e, i, o, u*).

For example, for two double bonds, suffix is ***diene*** and if it is to be added to word root but (for 4C atoms), it becomes butadiene.

(b) **Secondary suffix.** *It indicates the presence of functional group in the organic compound.* Some common secondary suffixes used to represent functional groups are :

Class of organic compound	Functional group	Secondary suffix
Alcohols	–OH	–ol
Aldehydes	–CHO	–al
Ketones	>C = O	–one
Carboxylic acids	–COOH	–oic acid
Esters	–COOR	alkyl ..... oate
Acid chlorides	–COCl	–oyl chloride
Acid amides	$–CONH_2$	–amide
Nitriles	–C ≡ N	–nitrile
Amines	$–NH_2$	–amine

It may be noted that while adding the secondary suffix to the primary suffix, the terminal *'e'* of the primary suffix (*i.e., ane, ene* or *yne*) is **dropped** if the complete secondary suffix (the suffix plus multiplying affix, if any, such as di, tri, tetra) begins with a vowel (*a, e, i, o, u*). However, the terminal *'–e'* is **retained** if the secondary suffix begins with a consonant.

For example,

$CH_3—CH_2—CH_2—CH_2—OH$ has **word root** but
pri. suffix ane
sec. suffix -ol

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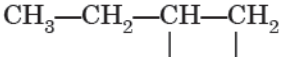
So, its name is But + ane + ol = Butanol or Butan-1-ol

[Here, **e** of ane is dropped because sec. suffix -ol begins with a vowel. Please note 1 before -ol indicates the position of the sec. suffix discussed later on].



has		
	word root	but
	pri. suffix	ane
	complete sec. suffix	diol

So, its name is But + ane + diol = Butanediol or **Butane -1, 2-diol**

[Here **e** of ane is not **dropped** because complete sec–suffix (diol) begins with a consonant; 1– and 2– before diol indicate the positions of the sec–suffix, –OH groups].

(*iii*) **Prefixes.** *There are many groups which are not regarded as functional groups in the IUPAC name of the compound.* These are regarded as **substituents** or **side chains.** These are represented as **prefixes** and are placed before the word root while naming a particular compound. These may be :

(a) **Alkyl groups.** These groups contain one hydrogen atom less than the alkane. These are named by substituting the suffix **ane** of the name of the corresponding alkane by **yl.**

i.e. alkane – ane + yl = **alkyl.**

For example,

CH_4	:	Methane	becomes	CH_3-	:	Methyl
CH_3CH_3	:	Ethane	becomes	CH_3CH_2-	:	Ethyl
$CH_3\ CH_2CH_3$	:	Propane	becomes	$CH_3CH_2CH_2-$	:	Propyl etc.

(b) **Functional groups not regarded as principal functional groups.** If a compound contains more than one functional group, then one of the functional group is regarded as principal functional group and is treated as secondary suffix. The other functional groups are regarded as substituents and are indicated by prefixes. This is discussed later in this chapter.

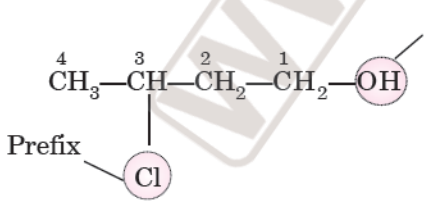
Some common prefixes are given below :

Substituent	Prefix	Substituent	Prefix
—F	Fluoro	—NO	Nitroso
—Cl	Chloro	—N=N—	Diazo
—Br	Bromo	$-OCH_3$	Methoxy
—I	Iodo	$-OC_2H_5$	Ethoxy
$-NO_2$	Nitro	—OH	Hydroxo
$-NH_2$	Amino		

Thus, a complete IUPAC name of an organic compound may be represented as :

Prefix + Word root + Primary suffix + Secondary suffix.

For example, the following compound has a chain of four carbon atoms (word root is **but**). It contains only C–C bond (primary suffix is **–ane).** It contains functional group –OH at C–1 (secondary suffix is **-ol**). It also contains a substituent Cl at C–3 (prefix is **chloro**).



Word root : But
Primary suffix : -ane
Secondary suffix : -ol
Prefix : –Chloro

IUPAC name : Chloro + but + ane + ol
3–Chlorobutan-1-ol

The *e* of –ane is dropped because it is followed by *o* (vowel). Numbers 1 and 3 represent the positions of suffix and prefix.

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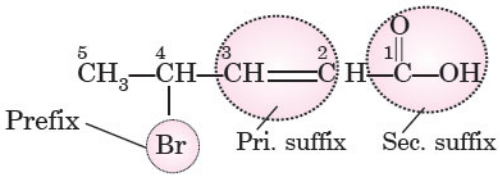
Let us consider the following compound. It has a chain of five carbon atoms having functional group —COOH. It also contains a double bond at C–2 and a substituent (–Br) at C–4.



Word root : Pent (five C–C–C–C–C)
Primary suffix : ene (double bond at C–2)
Secondary suffix : oic acid (–COOH group)
Prefix : Bromo (–Br group at C–4)

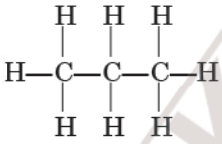
IUPAC name : Bromo + pent + ene + oic acid
or **4–Bromopent–2–en–1–oic acid**

Representation of Organic Compound

An organic compound may be represented by *its molecular formula, structural formula* or *graphic formula.* For example, propane molecule may be represented as :

C_3H_8
Molecular formula

$CH_3—CH_2—CH_3$
Structural formula


Graphic formula

Structural formula is often used to represent an organic compound. Some time the structural formula is written without bonds *e.g.,* propane may be written as $CH_3CH_2CH_3$. This is also known as *condensed structural formula.*

Before taking up the IUPAC nomenclature of different compounds, let us study common and IUPAC names of some common classes of organic compounds.

Different Classes of Organic Compounds

1. Hydrocarbons

These are the organic compounds containing *carbon* and *hydrogen* atoms only. They may be further classified into two classes : *saturated* and *unsaturated hydrocarbons.*

(a) Saturated Hydrocarbons — Alkanes

General formula = $C_n H_{2n+2}$ *Suffix :* **ane**

These are the organic compounds which contain only carbon—carbon single bonds. These were earlier named as *paraffins* (Latin : meaning *little affinity*) due to their least chemical reactivity. According to IUPAC system, these are named as *alkanes* (**ane** is suffix with word root). Various members of the series are given below :

Formula	IUPAC name	Common name
CH_4	Methane	Methane
CH_3CH_3	Ethane	Ethane
$CH_3CH_2CH_3$	Propane	Propane
$CH_3CH_2CH_2CH_3$	Butane	*n*-Butane
$CH_3(CH_2)_3CH_3$	Pentane	*n*-Pentane
$CH_3(CH_2)_4CH_3$	Hexane	*n*-Hexane

Classification of carbon atoms in alkanes. The carbon atoms in an alkane molecule may be classified into four types as *primary* (1°), *secondary* (2°), *tertiary* (3°) and *quaternary* (4°).

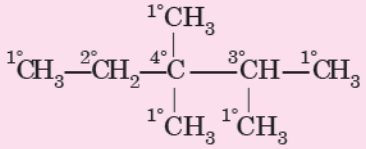
(*i*) A carbon atom attached to one other (or no other) carbon is called primary carbon (written as 1° carbon).

(*ii*) A carbon atom attached to two other carbon atoms is called secondary carbon (written as 2° carbon).

(*iii*) A carbon atom attached to three other carbon atoms is called tertiary carbon (written as 3° carbon).

(*iv*) A carbon atom attached to four other carbon atoms is called quaternary carbon (written as 4° carbon).

Hydrogen atoms attached to 1°, 2° and 3° carbon atoms are referred to as primary, secondary and tertiary H atoms respectively. The following example, clearly differentiates the various carbon atoms.



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Alkyl radical

The alkanes are also represented by the general formula RH where R is called the *alkyl group* or *radical* and has the formula C_nH_{2n+1}. The alkyl group, therefore, contains only one H atom less than the alkane. The alkyl group is named by substituting the suffix **'ane'** of the name of the corresponding alkane by 'yl'. (alkane—ane + yl = alkyl). For example,

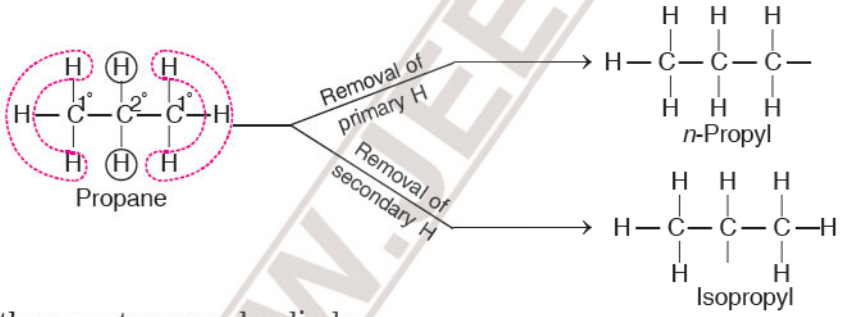
CH_4, Methane	becomes	CH_3—	Methyl
CH_3CH_3, Ethane	becomes	CH_3CH_2—	Ethyl

Alkyl radical	Corresponding alkane	Name
CH_3—	CH_4	Methyl
CH_3CH_2—	C_2H_6	Ethyl
$CH_3CH_2CH_2$—	C_3H_8	Propyl
$CH_3CH_2CH_2CH_2$—	C_4H_{10}	Butyl
$CH_3CH_2CH_2CH_2CH_2$—	C_5H_{12}	Pentyl
$CH_3(CH_2)_8\ CH_2$—	$C_{10}H_{22}$	Decyl

It may be noted that there is one methyl radical and one ethyl radical. However, there are two propyl radicals depending upon the nature of H atom removed. There are two types of carbon atoms in propane; the two end carbon atoms are primary (attached to only one other carbon atom) while the middle carbon is secondary (attached to two other carbon atoms). The removal of hydrogen may occur as :

(*i*) The six primary H atoms shown within dotted lines in the formula are equivalent (1°). Removal of any one of these six H atoms gives an alkyl radical called *normal* propyl group or simply written as *n*-propyl.

(*ii*) Removal of one of the two secondary H atoms shown within solid circles in the formula for propane gives different propyl group called *isopropyl* group.

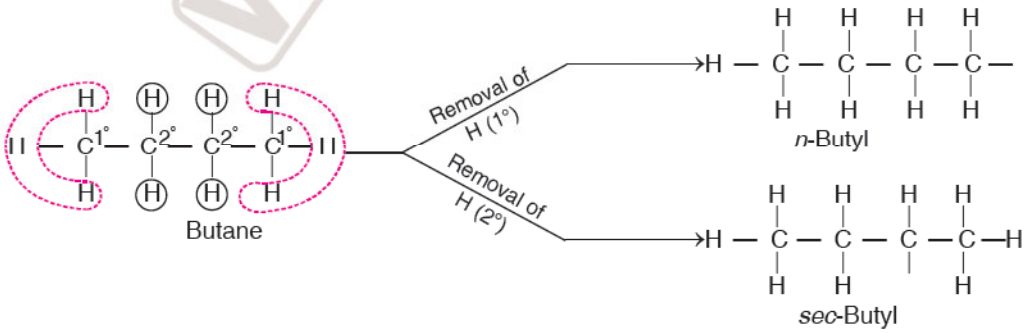


Thus, there are two propyl radicals :

$CH_3CH_2CH_2$—
n-Propyl

CH_3CHCH_3
|
Isopropyl

Similarly, butane gives four butyl radicals (two from *n*-butane and two from isobutane) as



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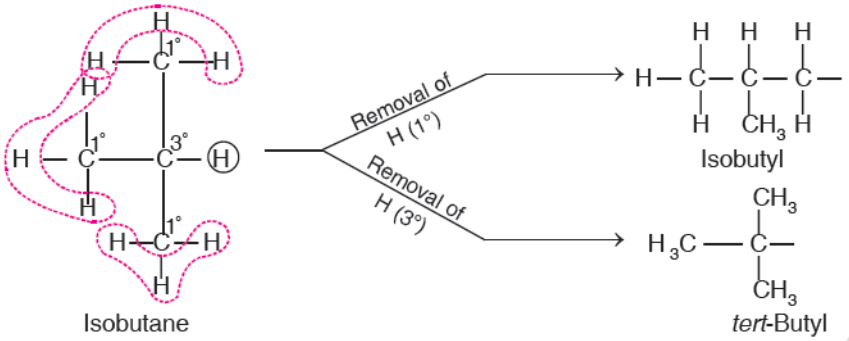
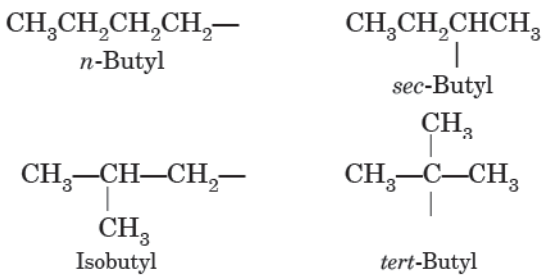
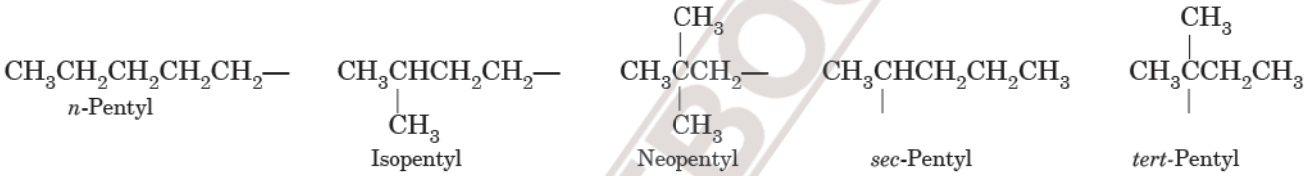


Isobutane

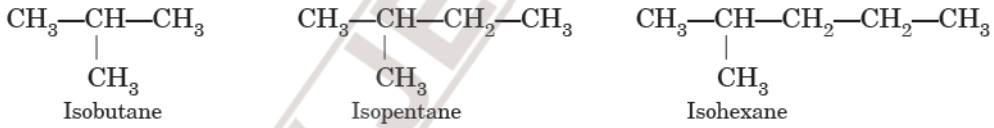
Thus, there are four butyl groups, namely



Similarly, removal of different H atoms in pentane gives the following radicals :



The prefix *sec*- or *tert*-before the name of the group indicate that the H atom was removed from a secondary or tertiary carbon atom respectively. It may be noted that an *iso* compound is one which has methyl group attached to second last carbon atom of the continuous chain (discussed later). For example,



Thus, the number of different alkyl groups produced from an alkane depends upon how many types of H atoms (primary, secondary or tertiary) can be replaced.

NOTE

It may be noted that *sec*- and *tert*-compounds are written with a dash between *sec* or *tert* and name of the alkyl group. For example, *sec*-Butyl, *tert*-Butyl etc. However, *iso* or *neo* compounds are written as one word. For example, isobutane, neopentane, etc.

Abbreviations for alkyl groups

It may be noted that some of the alkyl groups are also written using abbreviations. For example, methyl group is written as Me. The common abbreviations for the alkyl groups are :

Alkyl group		Abbreviation
CH_3 –	Methyl	Me –
CH_3CH_2 –	Ethyl	Et –
$CH_3CH_2CH_2$ –	Propyl	Pr –
$CH_3CH_2CH_2CH_2$ –	Butyl	Bu–

***(b)* Unsaturated hydrocarbons.** These are hydrocarbons which contain carbon to carbon double bonds ($>C=C<$) or carbon to carbon triple bonds (—C ≡ C—) in their molecules. These are further classified into two types : *alkenes* and *alkynes*.

***(i)* Alkenes :** *General formula : C_nH_{2n} Suffix :* **ene**

The molecules containing one carbon-carbon double bond are called alkenes. They have the general formula C_nH_{2n}. These were previously called olefins (in Greek *olefiant—oil forming*) because the lower gaseous members of the family form oily products when treated with chlorine.

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In IUPAC system, the name of alkene is derived by replacing suffix **ane** of the corresponding alkane by **ene**. For example,

$CH_3—CH_3$ Ethane (Alkane) $\qquad$ $H_2C = CH_2$ Ethene (Alkene)

In higher alkenes, the position of the double bond can be indicated by assigning numbers 1, 2, 3, 4, ... to the carbon atoms present in the molecule. The position is mentioned by the first carbon of the double bond. The number is written immediately before the part of the name to which it belongs. For example,

$CH_2 = CH—CH_2—CH_3$ But–1–ene (Not But–3–ene) $\qquad$ $CH_3—CH = CH—CH_2—CH_3$ Pent–2–ene (Not Pent–3–ene)

The IUPAC names of first six members of the family are given below. The common names* are also given below :

Alkene	Common name	IUPAC name
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3CH = CH_2$	Propylene	Propene
$CH_3CH_2CH = CH_2$	α-Butylene	But-1-ene
$CH_3CH = CHCH_3$	β-Butylene	But-2-ene
$CH_3.(CH_2)_2CH = CH_2$	α-Pentylene	Pent-1-ene
$CH_3CH_2.CH = CH.CH_3$	β-Pentylene	Pen-2-ene
$CH_3(CH_2)_3CH = CH_2$	α-Hexylene	Hex-1-ene
$CH_3(CH_2)_2CH = CHCH_3$	β-Hexylene	Hex-2-ene
$CH_3CH_2CH = CHCH_2CH_3$	γ-Hexylene	Hex-3-ene

***(ii)* Alkynes :** *General formula* : C_nH_{2n-2} Suffix : **yne**

Alkynes are the unsaturated hydrocarbons with a triple bond (—C ≡ C—). They are represented by the general formula C_nH_{2n-2}.

Alkynes are named in the same way as alkenes *i.e.,* by replacing suffix **ane** of alkane by **yne**. In higher members, the position of triple bond is indicated by giving numbers 1, 2, 3, 4, ... etc. to the carbon atom in the molecule. The numbering of the chain is always done from one end in such a manner that the triple bonded carbon atom gets the least number, as indicated in alkenes. For example,

$CH_3—C \equiv CH$ Prop-1-yne (Not Prop-2-yne) $\qquad$ $CH_3—CH_2—C \equiv CH$ But-1-yne (Not But-3-yne) $\qquad$ $CH_3—C \equiv C—CH_3$ But-2-yne

The IUPAC and the common names of a few important members of the family are given below :

Alkyne	Common name	IUPAC name
$HC \equiv CH$	Acetylene	Ethyne
$H_3C—C \equiv CH$	Methyl acetylene (Allylene)	Propyne
$H_3C—C \equiv C—CH_3$	Dimethyl acetylene	But–2–yne
$H_3C—CH_2—C \equiv CH$	Ethyl acetylene	But–1–yne
$H_3C—(CH_2)_2—C \equiv CH$	*n*–Propyl acetylene	Pent–1–yne
$H_3C—CH_2—C \equiv C—CH_3$	Ethyl methyl acetylene	Pent–2–yne
$H_3C—(CH_2)_3—C \equiv CH$	*n*–Butyl acetylene	Hex–1–yne
$H_3C—(CH_2)_2—C \equiv C—CH_3$	Methyl *n*-propyl acetylene	Hex–2–yne
$H_3C—CH_2—C \equiv C—CH_2—CH_3$	Diethyl acetylene	Hex–3–yne

2. Alkyl halides (Halogen derivatives of alkanes)

Halogen derivatives of alkanes are called **alkyl halides** or **haloalkanes**

These are obtained from alkanes by the replacement of one or more hydrogen atoms by halogen atoms :

$$RH \xrightarrow{-H, +X} RX \ (X = F, Cl, Br, I)$$

$$C_2H_6 \xrightarrow{-H, +Cl} C_2H_5Cl$$

*The common names of alkenes are derived from corresponding alkanes by replacing the suffix *ane* of alkane by *ylene* as ethylene, propylene, butylene etc. In higher alkenes, sometimes the carbon atoms are indicated as α, β, γ, δ ..... so that the position of double bond can be correctly mentioned. For example,

$\overset{\delta}{CH_3}—\overset{\gamma}{CH_2}—\overset{\beta}{CH} = \overset{\alpha}{CH_2}$ α-Butylene $\qquad$ $\overset{\delta}{CH_3}—\overset{\gamma}{CH} = \overset{\beta}{CH}—\overset{\alpha}{CH_3}$ β-Butylene

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These are further classified as *mono-*, *di* -, *tri–* and *tetrahaloalkanes*, etc. according as they contain one, two, three, four etc. halogen atoms respectively in their molecules.

(a) Monohaloalkanes

General formula : $C_n H_{2n+1}X$ or RX *Prefix* : **Halo**

These are derived from alkanes by replacing one hydrogen atom by halogen atom. The common names of these are derived by adding the word halide (fluoride, chloride, bromide or iodide) to the name of the alkyl group *i.e.* alkyl + halide = **alkyl halide**.

In the IUPAC system, they are named as halogen substituted alkanes *i.e.*, **haloalkanes**. Thus, the name of halogen compound is given by prefixing *fluoro, chloro, bromo* or *iodo* to the name of the alkane. The position of the halogen atom is also indicated by giving the number of C atom to which halogen is attached.

Structural formula	Common name	IUPAC name
CH_3Cl	Methyl chloride	Chloromethane
CH_3CH_2Cl	Ethyl chloride	Chloroethane
$CH_3\underset{\displaystyle I}{\underset{\vert}{C}}HCH_3$	Isopropyl iodide	2-Iodopropane
$CH_3\underset{\displaystyle Br}{\underset{\vert}{C}}H—CH_2—CH_3$	*Sec*-butyl bromide	2-Bromobutane
$CH_3CH_2CH_2CH_2I$	*n*-Butyl iodide	1-Iodobutane

(b) Dihaloalkanes

Alkanes containing two halogen atoms per molecule are called **dihaloalkanes**.

General formula : $C_n H_{2n}X_2$ *Prefix* : **Dihalo**

The dihalogen derivatives have special common names depending upon whether the halogen atoms are present on the same or different carbon atoms. In IUPAC system, all types of dihalides are called dihaloalkanes, the positions of the halogen atoms being indicated by lowest possible numbers. These are commonly named according to IUPAC systems. These can be divided into three types as:

(i) **Alkylidene halides :** When both halogen atoms are attached to the same C-atom, these are called **alkylidene dihalides** or simply **alkylidene halides.** These are also called **gem dihalides** or simply **gem halides**.

CH_3CHCl_2
Ethylidene dichloride
(gem-dihalide)

$CH_3-\underset{\displaystyle Cl}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-Cl$
Isopropylidene dichloride

$CH_3CH_2CHCl_2$
Propylidene dichloride

IUPAC : 1, 1-Dichloroethane **IUPAC :** 2, 2-Dichloroethane **IUPAC :** 1, 1-Dichloropropane

(ii) **Alkylene halides :** When the two halogen atoms are attached to adjacent C-atoms, they are called **alkylene dihalide** or simply **alkylene halide.** These are also called **vicinal dihalides** or simply **vic-halides.** For example,

$\underset{\displaystyle Cl}{\underset{\vert}{CH_2}}—\underset{\displaystyle Cl}{\underset{\vert}{CH_2}}$
Ethylene dichloride
(vic-dihalide)

$CH_3—\underset{\displaystyle Cl}{\underset{\vert}{CH}}—\underset{\displaystyle Cl}{\underset{\vert}{CH_2}}$
Propylene dichloride

$CH_3-\underset{\displaystyle Br}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-CH_2Br$
Isobutylene dibromide

IUPAC : 1, 2-Dichloroethane **IUPAC :** 1, 2-Dichloropropane **IUPAC :** 1, 2-Dibromo-2-methylpropane

(iii) **Polymethylene dihalides :** When the same two halogen atoms are present on the terminal carbon atoms of alkanes (containing three or more carbon atoms) *i.e.*, α, ω positions of the carbon chain, they are called **polymethylene dihalides.** For example,

$ClCH_2CH_2CH_2CH_2Cl$
Tetramethylene dichloride
IUPAC : 1, 4-Dichlorobutane

$BrCH_2CH_2CH_2Br$
Trimethylene dibromide
IUPAC : 1, 3-Dibromopropane

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The common and IUPAC names of some dihaloalkanes are given below :

Structure	Common name	IUPAC name
CH_2Cl_2	Methylene chloride	Dichloromethane
$^1CH_2Br$ | $^2CH_2Br$	Ethylene dibromide	1, 2-Dibromoethane
$^2CH_3$ | $^1CHBr_2$	Ethylidine dibromide	1, 1-Dibromoethane
$CH_2—CH_2—CH_2$ | | Cl Cl	Trimethylene dichloride (α, γ)	1, 3-Dichloropropane
$CH_3CH_2CHCl_2$	Propylidene dichloride	1, 1-Dichloropropane
$CH_3—CH—CH_2$ | | Cl Cl	Propylene dichloride	1, 2 - Dichloropropane
$CH_3—C—CH_3$ Cl Cl	Isopropylidene dichloride	2, 2 - Dichloropropane

(c) Polyhaloalkanes

The **general formula** of trihaloalkanes is $C_nH_{2n-1}X_3$ while that of tetrahaloalkanes is $C_nH_{2n-2}X_4$.

There are no systematic common names for tri-and tetrahaloalkanes. However, trihalomethanes are known by their trivial names *i.e.* **haloforms** and tetrahalomethanes as **carbon tetrahalides**.

These are commonly named according to IUPAC system.

$CHCl_3$	CHI_3	CCl_4
Chloroform	Iodoform	Carbon tetrachloride
IUPAC : Trichloromethane	**IUPAC :** Triiodomethane	**IUPAC :** Tetrachloromethane

Fully halogenated hydrocarbons are also called **perhalohydrocarbons** (per means that all the hydrogens of the hydrocarbon are replaced by halogen atoms). It may be noted that polyhaloalkanes and other complex halogen compounds are named according to IUPAC system.

($CF_3—CF_2—CF_3$) : Perfluoropropane **IUPAC :** Octafluoropropane

The common and IUPAC names of some tri- and tetrahaloalkanes are given below:

Structure	Common name	IUPAC name
$CHCl_3$	Chloroform	Trichloromethane
CHI_3	Iodoform	Triiodomethane
$CHBr_3$	Bromoform	Tribromomethane
$CH_3—CCl_3$	—	1, 1, 1 – Trichloroethane
$ClCH_2—CHCl_2$	—	1, 1, 2 – Trichloroethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$Br_2CH—CHBr_2$	Acetylene tetrabromide	1, 1, 2, 2 – Tetrabromoethane

3. Alcohols or alkanols

General formula : $\mathbf{C_n\ H_{2n+1}\ OH}$ **or ROH**

Functional group : —OH *Secondary suffix*: **ol**

These are derived by replacing one hydrogen atom from an alkane by one hydroxyl group. In the IUPAC system, these are called **alkanols** and their names have been derived by changing *–e* of the corresponding alkane by **–ol (alkane –e + ol = alkanol).**

Molecules having more than one —OH groups are called *diols* (2—OH groups), *triols* (3—OH groups) etc.

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Formula	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3CH(OH)CH_3$	Isopropyl alcohol	Propan-2-ol
$CH_3(CH_2)_2CH_2OH$	*n*-Butyl alcohol	Butan–1–ol
$CH_3CH(OH)CH_2CH_3$	*sec*-Butyl alcohol	Butan–2–ol
$CH_2(OH)—CH_2(OH)$	Ethylene glycol	Ethane–1, 2–diol
$CH_2(OH)—CH(OH)—CH_3$	Propylene glycol	Propane–1, 2–diol
$HOCH_2—CH_2—CH_2OH$	Trimethylene glycol	Propane -1, 3-diol
$CH_2(OH)—CH(OH)—CH_2(OH)$	Glycerol or Glycerine	Propane - 1, 2, 3 - triol

4. Ethers or Alkoxyalkanes

General formula : $C_mH_{2m+1}OC_nH_{2n+1}$ or ROR′ $m = n$ or $m \neq n$

Functional group : —O— *Prefix* : **alkoxy**

These are derived from alkanes by replacing one hydrogen atom by alkoxy group (—OR). For example, methoxy (OCH_3), ethoxy (OC_2H_5) or propoxy (OC_3H_7). In an ether molecule, two alkyl radicals are linked on either sides to a divalent oxygen atom (—O—). They are called simple ethers if R = R′ (*e.g.,* CH_3OCH_3) and mixed ethers if R and R′ are different (*e.g.,* $CH_3OC_2H_5$). In the IUPAC system, ethers are called **alkoxyalkanes**. The alkoxy group is taken with smaller alkyl group.

Ether	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OC_2H_5$	Ethyl methyl ether	Methoxyethane

It may be noted that *the last compound is not ethoxy methane because alkoxy group is taken with lesser number of C atoms.*

5. Aldehydes or Alkanals

General formula : $C_nH_{2n+1}CHO$ (where *n* can be 0 also *e.g.,* HCHO)

Functional group : $-C(=O)H$ *Secondary suffix* : **al**

These compounds are obtained by replacing a hydrogen atom attached to the terminal carbon atom in alkane molecule by an aldehydic (CHO) group. The first member is, however, obtained by replacing a hydrogen atom in the hydrogen molecule.

These are called **alkanals** in the IUPAC system of nomenclature and the names of individual members are derived by changing *–e* of corresponding alkane by **–al (alkane –e + al = alkanal).**

Note : In aldehydes, the —CHO group is always present at the end of the chain and there is no need to designate its position as 1.

While counting the carbon atoms in the parent chain, the carbon of the —CHO group is also counted. For example, the parent chain in $CH_3CH_2CH_2CHO$ corresponds to 4C atoms and not 3. Further, it should be simply named as butanal and not butan-1-al because —CHO is always terminal.

Aldehyde	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3CH_2CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2CHO$	*n*-Butyraldehyde	Butanal

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6. Ketones or Alkanones

General formula : $C_nH_{2n+1}COC_mH_{2m+1}$ or RCOR′

Functional group : $>C=O$ *Secondary suffix :* **one**

These are obtained by replacing two hydrogen atoms attached to the *non-terminal* carbon atom in alkane molecule by a divalent oxygen atom. Thus the functional group called **ketonic group** ($>C=O$) contains a carbon atom joined to the oxygen atom by double bond. To the either sides of the functional group carbon atom, alkyl radicals are attached.

The ketones are called *simple ketones* when R = R′ (*e.g.,* CH_3COCH_3) and *mixed ketones* if R and R′ are different (*e.g.,* $CH_3COC_2H_5$). In the IUPAC system, ketones are called **alkanones.** The names of individual members are derived by replacing *–e* of the corresponding alkane by **-one** (**alkane – e + one = alkanone**).

Ketone	Common name	IUPAC name
$CH_3—\overset{\overset{O}{\|}}{C}—CH_3$	Dimethyl ketone (Acetone)	Propanone
$CH_3—\overset{\overset{O}{\|}}{C}—CH_2CH_3$	Ethyl methyl ketone	Butan-2-one
$C_2H_5—\overset{\overset{O}{\|}}{C}—CH_2CH_3$	Diethyl ketone	Pentan-3-one
$CH_3—\overset{\overset{O}{\|}}{C}—CH_2CH_2CH_3$	Methyl-*n*-propyl ketone	Pentan-2-one

The prefix 2 or 3 indicates the position of the functional group carbon atom which must always get the lowest possible number.

7. Monocarboxylic acids or Alkanoic acids

General formula : $C_nH_{2n+1}—COOH$ (where *n* can be zero also)

Functional group : $—\overset{\overset{O}{\|}}{C}—OH$ *Scondary suffix* : **oic acid**

In these compounds, one hydrogen atom in alkane molecule is replaced by a carboxyl (COOH) group. The first member is, however, obtained by replacing a hydrogen atom in the hydrogen molecule.

In the IUPAC system, they are called **alkanoic acids** and are named by replacing the terminal **–e** of the corresponding alkane by **–oic acid (alkane –e + oic acid = alkanoic acid)**

Monocarboxylic acid	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	*n*-Butyric acid	Butanoic acid
$CH_3CH_2CH_2CH_2COOH$	*n*-Valeric acid	Pentanoic acid

8. Acid halides or acyl halides or alkanoyl halides

General formula : $C_nH_{2n+1}COX$ or RCOX (where *n* can be zero also)

Functional group : $—\overset{\overset{O}{\|}}{C}—X$ (halocarbonyl) *Secondary suffix* : **oyl halide**

These are derivatives of carboxylic acids in which —OH group of a carboxylic acid has been replaced by a halogen atom. Among these acyl chlorides (RCOCl) are more common because these are more stable and easy to handle.

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The common names are derived from the common names of the acid by replacing ***ic acid*** by ***yl halide*** **as acetic acid-*ic* acid + *yl* halide = acetyl halide**

The IUPAC names are also derived by replacing **–*ic acid*** of the name of acid **by *yl* and adding the name of the halide.** Alternatively, the name is derived by replacing terminal **–*e*** of the corresponding alkane by the suffix ***oyl halide*** as :

Alkane – e + oyl halide = Alkanoyl halide

Acid halide	Common name	IUPAC name
HCOCl (unstable)	Formyl chloride	Methanoyl chloride
CH_3COCl	Acetyl chloride	Ethanoyl chloride
CH_3CH_2COCl	Propionyl chloride	Propanoyl chloride
$CH_3CH_2CH_2COCl$	*n*–Butyryl chloride	Butanoyl chloride

9. Acid anhydrides

General formula : $R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$ or $(RCO)_2O$

where R and R′ may be same or different alkyl groups.

Functional group : $-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$ *Secondary suffix* : **anhydride**

These are also acid derivatives which are derived from carboxylic acids by the removal of water from two molecules of the acid.

$$R-\overset{\overset{O}{\|}}{C}-\boxed{OH + H}\ O-\overset{\overset{O}{\|}}{C}-R \xrightarrow{-H_2O} R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$$

The common or IUPAC names are obtained by replacing the word **acid** of the common name or IUPAC name of the carboxylic acid by the word **anhydride**.

Symmetrical anhydrides of substituted carboxylic acids are named by adding the word ***bis*** to the name to indicate that two identical groups are present. However, unsymmetrical anhydrides are named by writing the names of the two acids alphabetically before the word anhydride.

Acid anhydride	Common name	IUPAC name
$CH_3COOCOCH_3$	Acetic anhydride	Ethanoic anhydride
$CH_3CH_2COOCOCH_2CH_3$	Propionic anhydride	Propanoic anhydride
$CH_3COOCOC_2H_5$	Acetic propionic anhydride	Ethanoic propanoic anhydride
$(ClCH_2CO)_2O$	*Bis*(chloro acetic anhydride)	*Bis*(chloroethanoic anhydride)

10. Esters

General formula : $R-\overset{\overset{O}{\|}}{C}-O-R'$ Where R = H or any alkyl group and R′ is always an alkyl group

Functional group : $-\overset{\overset{O}{\|}}{C}-OR'$

Secondary prefix : **alkyl**

Secondary suffix : **oate**

These are the derivatives of carboxylic acids in which —OH group of the carboxylic acid has been replaced by —OR group (where R is alkyl).

The common or IUPAC names are obtained by prefixing the name of **alkyl group** (OR′ part) before the name of the parent acid and changing the suffix ***ic acid*** to ***oate***.

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Ester	Common name	IUPAC name
$HCOOCH_3$	Methyl formate	Methyl methanoate
$HCOOC_2H_5$	Ethyl formate	Ethyl ethanoate
CH_3COOCH_3	Methyl acetate	Methyl ethanoate
$CH_3COOC_2H_5$	Ethyl acetate	Ethyl ethanoate

11. Acid amides or alkanamides

General formula : $RCONH_2$ (R may be H or any alkyl group)

Functional group : $-\overset{\overset{O}{\|}}{C}-NH_2$ (amide) *Secondary suffix* : **amide**

These are derivatives of carboxylic acids in which —OH group of a carboxylic acid has been replaced by $—NH_2$ group.

The common names are derived by replacing ***ic acid*** from the common name of the corresponding acid by ***amide***.

The IUPAC names are derived by replacing ***ic acid*** of the name of the acid by ***amide*** or by replacing the ***–e*** of the name of the corresponding alkane by the suffix **amide (alkane – e + amide = alkanamide)**.

Acid amide	Common name	IUPAC name
$HCONH_2$	Formamide	Methanamide
CH_3CONH_2	Acetamide	Ethanamide
$CH_3CH_2CONH_2$	Propionamide	Propanamide

12. Amines

General formula : $C_nH_{2n+1} — NH_2$

Functional group : $—NH_2$; *Secondary suffix* : **amine**

These are the alkyl derivatives of ammonia. These are formed by replacing one, two or all the three hydrogen atoms in ammonia with alkyl radicals. In the IUPAC system, these are also called **alkanamines.** The name is derived by replacing **–e** of alkane by **amine**.

Amine	Common name	IUPAC name
CH_3NH_2	Methyl amine	Methanamine
$CH_3CH_2NH_2$	Ethyl amine	Ethanamine
$CH_3CH_2CH_2NH_2$	*n*-Propyl amine	Propanamine

13. Alkyl cyanides or alkanenitriles

General formula : $R—C\equiv N$

Functional group : $–C\equiv N$ (cyano or nitrile) *Secondary suffix* : **nitrile**

In the **common system,** the cyanides are named as alkyl cyanides and the suffix **cyanide** is added to the name of the alkyl group. These are also named on the basis of acid produced on their hydrolysis. In this case, the ending ***–ic acid*** of the acid is replaced by **onitrile** as

acetic acid – *ic acid* + onitrile = acetonitrile

According to IUPAC system, these are called **alkane nitriles** and the names are written by attaching the word **nitrile to the name of the alkane**. It may be noted that while counting the number of carbon atoms for a chain, carbon of –CN group is also counted in the chain.

Compound	Common name	IUPAC name
CH_3CN	Methyl cyanide or acetonitrile	Ethanenitrile
CH_3CH_2CN	Ethyl cyanide or propionitrile	Propanenitrile
$CH_3CH_2CH_2CN$	*n*-Propyl cyanide or butyronitrile	Butanenitrile
$CH_3CH(CH_3)CN$	Isopropyl cyanide or isobutyronitrile	2-Methylpropanenitrile

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14. Isocyanides or isonitriles or carbylamines

General formula : $R—N\equiv C$

Functional group : $—N\equiv C$ (isocyanide or isonitrile) *Secondary suffix* : **isocyanide or isonitrile**

In the **common system**, their name are derived by adding the suffix **carbylamine** or **isocyanide** to the name of the alkyl group.

There are no separate IUPAC names for isocyanides or isonitriles.

Compound	Common name
$CH_3—N\equiv C$	Methyl isocyanide or methyl carbylamine or methyl isonitrile
$C_2H_5—N\equiv C$	Ethyl isocyanide or ethyl carbylamine or ethyl isonitrile

15. Nitroalkanes

General formula : RNO_2

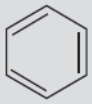
Functional group : $—NO_2$ or— $N\begin{matrix}\nearrow O\\ =O\end{matrix}$ group *Secondary prefix* **: nitro**

There are no common names for nitroalkanes. According to IUPAC system, these are named by prefixing *nitro* to the name of the parent alkane. The position of *nitro* group of the carbon chain is indicated by a number.

Compound	IUPAC name	Compound	IUPAC name
CH_3NO_2	Nitromethane	$^{3}CH_3—\overset{\overset{NO_2}{\vert}}{^{2}CH}—{}^{1}CH_3$	2-Nitropropane
$CH_3CH_2NO_2$	Nitroethane		
$^{3}CH_3\,^{2}CH_2\,^{1}CH_2NO_2$	1-Nitropropane		
$^{4}CH_3\,^{3}CH_2\,^{2}CH_2\,^{1}CH_2NO_2$	1-Nitrobutane	$^{4}CH_3—{}^{3}CH_2—\overset{\overset{NO_2}{\vert}}{^{2}CH}—{}^{1}CH_3$	2-Nitrobutane

The different classes of functional groups including multiple bonded compounds and the suffix or prefix required to name these compounds are given in Table 2. For illustration, one example of each family containing four carbon atoms is also given.

Table 2. Some of functional groups, classes of organic compounds and their nomenclature.

Class of compounds	Functional group	General formula	Suffix or Prefix	Examples
Alkenes	$\vert\ \vert$ $—C=C—$	*Suffix-ene* C_nH_{2n}	Replace 'ane' of alkane by 'ene'	$CH_3CH_2CH=CH_2$ But-1-ene $CH_3CH=CHCH_3$ But-2-ene
Alkynes	$—C\equiv C—$	C_nH_{2n-2}	*Suffix-yne* Replace 'ane' of alkane by 'yne'.	$HC\equiv CCH_2CH_3$ But-1-yne $H_3CC\equiv CCH_3$ But-2-yne
Arenes				 Benzene

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Haloalkanes	—X (X = F, Cl, Br, I)	RX	*Prefix-halo* named as haloalkanes	$CH_3CH_2CH_2CH_2Cl$ 1-Chlorobutane $CH_3CH(Cl)CH_2CH_3$ 2-Chlorobutane
Alcohols	—OH	R—OH	*Suffix-ol* Replace 'e' of alkane by 'ol'	$CH_3CH_2CH_2CH_2OH$ Butan-1-ol $CH_3CH_2CH(OH)CH_3$ Butan-2-ol
Thiols	–SH	R—SH	*Suffix – thiol* Replace 'e' of alkane by 'thiol'	$CH_3CH_2CH_2CH_2SH$ Butan - 1- thiol
Ethers	—O—	R—O—R′ (R' may be R)	*Prefix-alkoxy* named as 'alkoxy' alkane	$CH_3CH_2OCH_2CH_3$ Ethoxy ethane $CH_3OCH_2CH_2CH_3$ Methoxy propane
Aldehydes	$H-C(=O)-$	$R-C(=O)-H$	*Suffix-al* Replace 'e' of alkane by 'al'	$CH_3CH_2CH_2CHO$ Butanal
Ketones	$>C=O$	RCOR′	*Suffix-one* Replace 'e' of alkane by 'one'	$CH_3CH_2C(=O)CH_3$ Butan–2–one
Carboxylic acid	$HO-C(=O)-$	RCOOH	*Suffix-oic acid* Replace 'e' of alkane by 'oic' acid	$CH_3CH_2CH_2COOH$ Butanoic acid
Carboxylate ion	$—COO^-$	$RCOO^-$	*Suffix-oate* Replace 'ic' acid of the corresponding acid by 'oate'	$CH_3CH_2CH_2COO^-Na^+$ Sodium butanoate
Carboxylic acid derivatives				
(i) Acyl halides	$X-C(=O)-$ (X = Cl, Br, I)	RCOX	*Suffix*-oyl halide Replace *–ic* of the corresponding acid by *'yl'* halide	$CH_3CH_2CH_2COCl$ Butanoyl chloride
(ii) Esters	$RO-C(=O)-$	RCOOR′	Prefixing name of the alkyl group and replacing *'–ic'* acid of the corresponding acid by *'ate'*.	$CH_3CH_2COOCH_3$ Methyl propanoate
(iii) Amides	$NH_2-C(=O)-$	$RCONH_2$	*Suffix*—amide Replace *'oic'* acid of corresponding acid by 'amide'	$CH_3CH_2CH_2CONH_2$ Butanamide
(iv) Acid anhydrides	$—C(=O)—O—C(=O)—$	$R—C(=O)—O—C(=O)—R$	Add anhydride to the name of corresponding acid	$CH_3C(=O)—O—C(=O)CH_3$ Ethanoic anhydride

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Amines	$-NH_2$	RNH_2	*Suffix*—amine prefix *amino* named as 'amino alkane' or 'alkanamine'.	$CH_3CH_2CH_2CH_2NH_2$ Butan–1–amine
Cyanides	—CN	RCN	*Suffix*—nitrile Add nitrile after the name of alkane.	$CH_3CH_2CH_2CN$ Butanenitrile
Nitro	$-NO_2$	RNO_2	*prefix nitro* Add nitro before the name of alkane	$CH_3CH_2CH_2CH_2NO_2$ 1-Nitrobutane

GENERAL RULES FOR NAMING ORGANIC COMPOUNDS

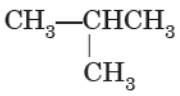
We have discussed the simple rules for naming organic compounds for different families. But many organic compounds have typical branching or substituents. Due to branching at different positions in a molecule, it is not possible to name them directly. The simple branched chain compounds can be named according to common names. **In the common system, all the isomeric alkanes (having same molecular formula) have the same parent name**. The names of various isomers are distinguished by prefixes. The prefix indicates the type of branching in the molecule. For example,

***(i)* Prefix n-**(*normal*) *is used for those alkanes in which all the carbon atoms form a continuous chain with no branching.*

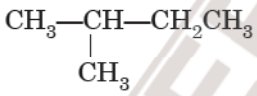
$CH_3CH_2CH_2CH_3$ — *n*-Butane

$CH_3CH_2CH_2CH_2CH_3$ — *n*-Pentane

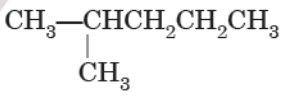
***(ii)* Prefix iso-** *is used for those alkanes in which one methyl group is attached to the next-to-end carbon atom (second last) of the continuous chain.*



Isobutane

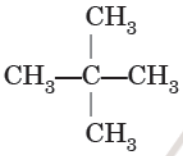


Isopentane

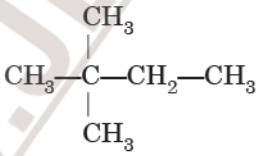


Isohexane

***(iii)* Prefix neo** *is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain.*



Neopentane



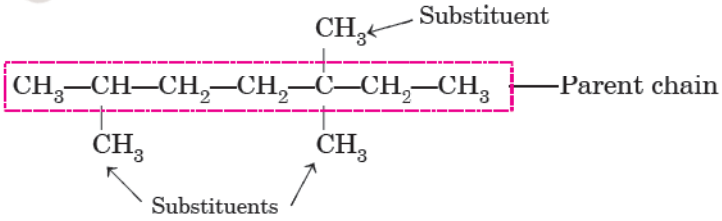
Neohexane

In naming highly branched alkanes, the system becomes complicated. However, they can be easily named according to IUPAC system as discussed below :

A. Rules for IUPAC Nomenclature of Branched Chain Saturated Hydrocarbons (Alkanes)

The following rules are used for naming the branched chain alkanes :

1. Longest chain rule. *Select the longest continuous chain of carbon atoms in the molecule*. The selected chain, containing the maximum number of carbon atoms, is regarded as the **parent** or **root chain** and it gives the name of the parent hydrocarbon. Carbon atoms which are not included in the parent chain are identified as *substituents* or *branched chains*.



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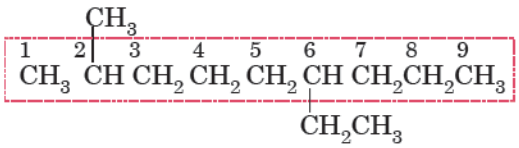
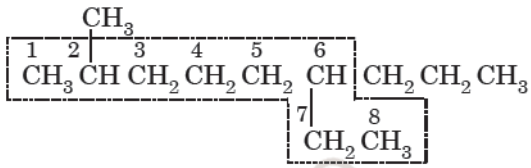
▶ *It may be noted that the longest chain may or may not be straight but it must be continuous.* For example, in the following compound, the parent chain consists of nine carbon atoms (structure I) and not eight (structure II). Thus, the compound is named as derivative of nonane.

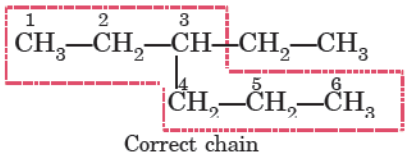


I
Correct chain
(contains 9 C atoms)

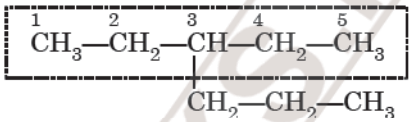


II
Wrong chain
(contains 8 C atoms)

Similarly, in the following example, the correct parent chain is of 6 C atoms.

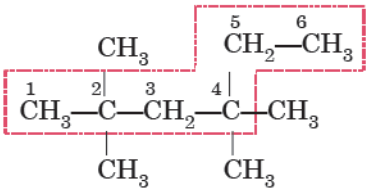


Correct chain
(contains 6C atoms)

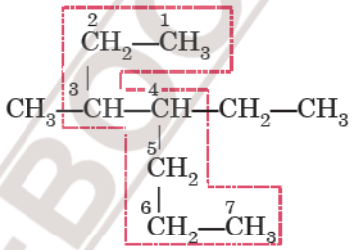


Wrong chain
(contains 5C atoms)

Some other examples indicating the proper choice of the parent chain are given below :

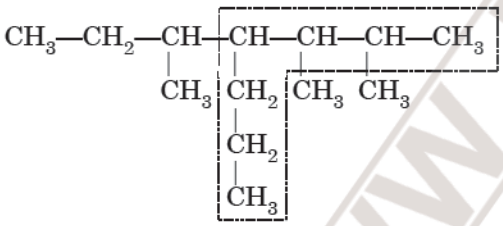


(Longest chain consists of six carbon atoms)

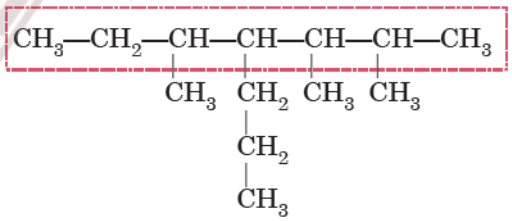


(Longest chain consists of seven C atoms)

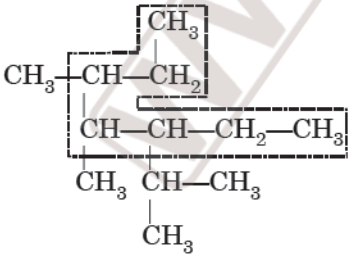
▶ *If two different chains of equal length are possible, the chain with maximum number of side chains or alkyl groups is selected.* For example,



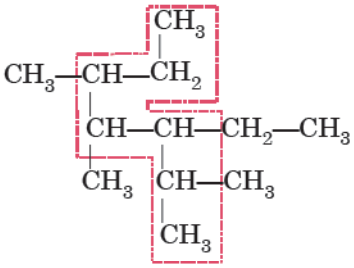
Not correct
(Longest chain but only 3-substituents)



Correct
(Longest chain with 4 substituents)



Not correct
(Longest chain but only 3 substituents)



Correct
(Longest chain with 4 substituents)

2. Position of the substituent. *Number the carbon atoms of the parent chain as 1, 2, 3... etc. starting from the end which gives lower number to the carbon atoms carrying the substituents.*

For example, if X represents a substituent, then the correct numbering of the carbon chain is as given in structure A. The numbering of the carbon chain as given in the structure B is ***wrong*** because it gives higher number to the carbon atom carrying the substituent.

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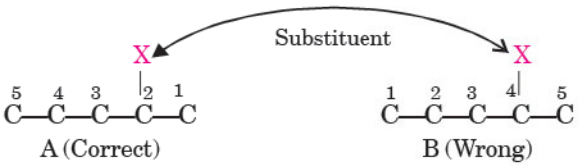
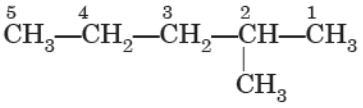
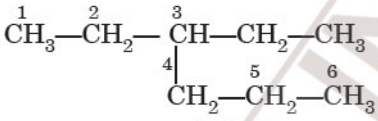


A (Correct) B (Wrong)

The number that indicates the position of the substituent or side chain is called **locant**. The position of the locant in the above structure is 2. *For naming the compound, the substituent group is written first with the number designating its location on the chain and the parent name is written last. The position number is written before the name of the substituent which is separated by a hyphen.* For example,



2-Methylpentane

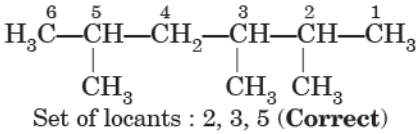


3-Ethylhexane

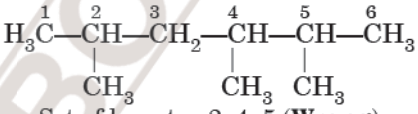
► *It must be remembered that numbers are separated from the groups by hyphens and there is no break between substituent and alkane names i.e., between methyl and pentane or ethyl and hexane.*

3. Lowest set of locants. *When two or more substituents are present, then end of the parent chain which gives the lowest set of the locants is preferred for numbering.*

This rule is called **lowest set of locants.** *This means that when two or more different sets of locants are possible, that set of locants which when compared term by term with other sets, each in order of increasing magnitude, has the lowest term at the first point of difference.* This rule is used irrespective of the nature of the substituent. For example,



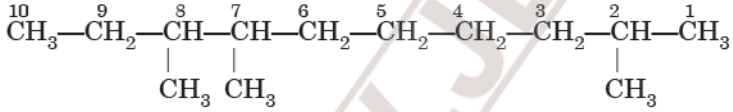
Set of locants : 2, 3, 5 (**Correct**)



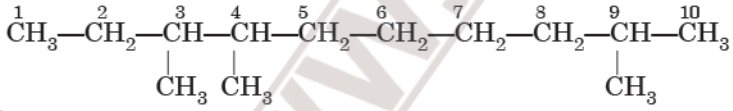
Set of locants : 2, 4, 5 (**Wrong**)

The correct set of locants is 2, 3, 5 and not 2, 4, 5. The first set is lower than the second set because at the **first difference** 3 is less than 4. (Note that first locant is same in both sets 2; 2 and the first difference is with the second locant 3, 4. We can compare term by term as 2-2, 3-4 (first difference), 5-5. **Only first point of difference is considered for preference).**

Similarly for the compound :



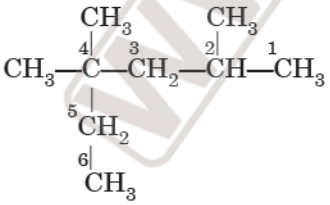
Set of locants : 2,7,8 (**Correct**)



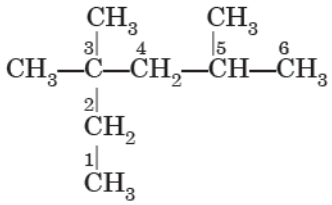
Set of locants : 3,4,9 (**Wrong**)

First set of locants 2, 7, 8 is lower than second set 3, 4, 9 because at the first point of difference 2 is lower than 3.

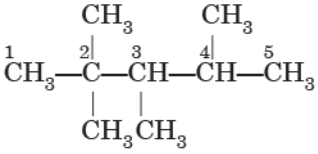
Similarly, the compounds given below should be numbered as indicated in structure A and not according to structure B.



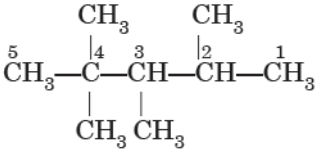
(A) Correct 2,4,4
Set of locants = 2,4,4



(B) Wrong
Set of locants = 3,3,5



(A) Correct
Set of locants = 2,2,3,4



(B) Wrong
Set of locants = 2,3,4,4

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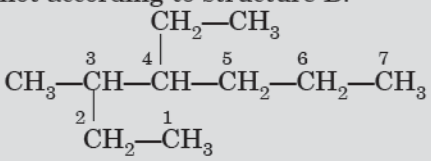
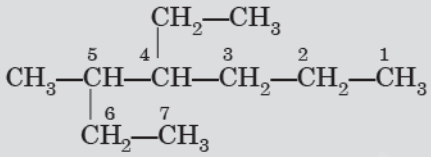
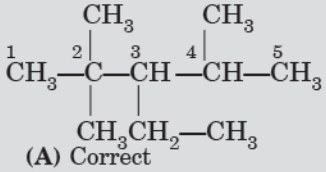
Lowest sum rule. It may be **noted** that earlier, the numbering of the parent chain containing two or more substituents was done in such a way that **sum of the locants is the lowest.** This rule is called **lowest sum rule**. For example, the carbon chain of alkanes given below should be numbered as indicated in structures A and not according to structure B.



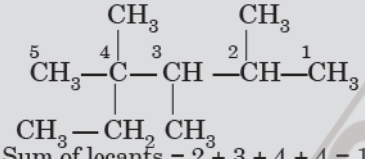
(A) Correct
Sum of locants = 3 + 4 = 7



(B) Wrong
Sum of locants = 4 + 5 = 9



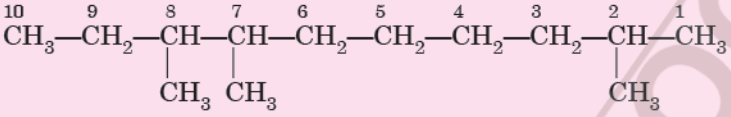
(A) Correct
Sum of locants = 2 + 2 + 3 + 4 = 11



Sum of locants = 2 + 3 + 4 + 4 = 13

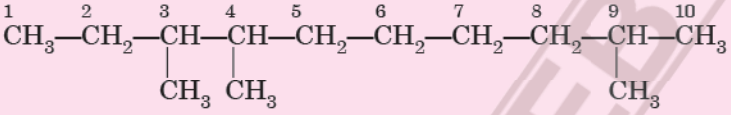
However, **according to latest IUPAC system of nomenclature, the lowest set of locants is preferred even if it violates the lowest sum rule.**

For example, if we consider the compound :



Set of locants = 2, 7, 8
Sum of locants = 2 + 7 + 8 = 17

Structure (A)

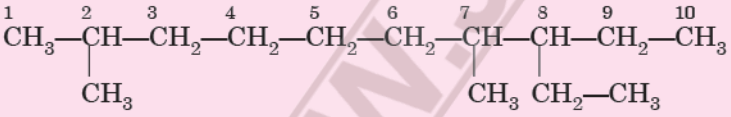


Set of locants : 3, 4, 9
Sum of locants = 3 + 4 + 9 = 16

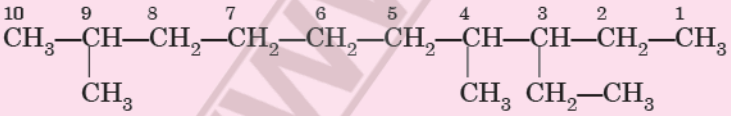
Structure (B)

This compound is numbered as 2, 7, 8 and not as 3, 4, 9 in accordance with latest lowest set of locants rule, even though it violates lowest sum rule.

Similarly, the correct set of locants of the following compound is 2, 7, 8 and not 3, 4, 9 even if it violates lowest sum rule.



Set of locants = 2, 7, 8
Sum of locants = 2 + 7 + 8 = 17

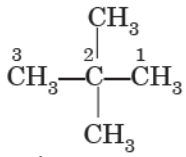


Set of locants = 3, 4, 9
Sum of locants = 3 + 4 + 9 = 16

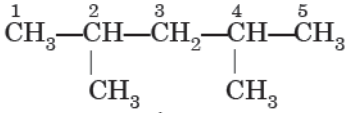
It must be emphasised that for simple alkanes, both the rules, lowest sum rule and lowest set of locants rule give the same name. However, differences are observed in case of names of complex or highly branched alkanes. So, **lowest set of locants rule should always be applied even if it violates lowest sum rule.**

4. Presence of more than one same substituent. *If the same substituent or side chain occurs more than once, the prefixes di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) ..... etc., are attached to the names of the substituents.*

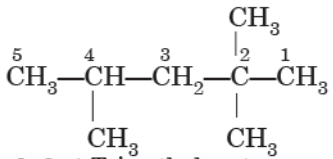
It may be noted that the *positions of the substituents are indicated separately and the numerals representing their positions are separated by commas.* For example,



2, 2-Dimethylpropane



2, 4-Dimethylpentane



2, 2, 4-Trimethylpentane

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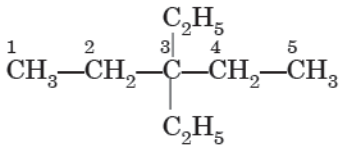
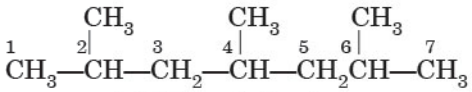


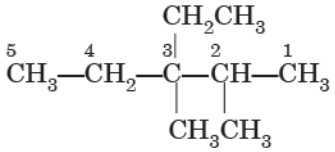
3, 3-Diethylpentane



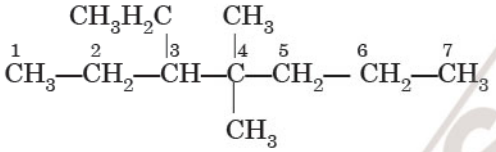
2, 4, 6-Trimethylheptane

5. Naming different substituents. *If two or more different substituents or side chains are present in the molecule, they are named in the alphabetical order along with their appropriate positions.*

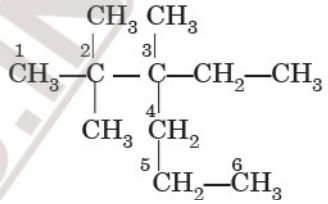
It must be remembered that the prefixes *di, tri* etc. are ignored while comparing the substituents.



3-Ethyl-2, 3-dimethylpentane



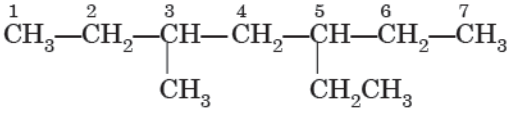
3-Ethyl-4, 4-dimethylheptane



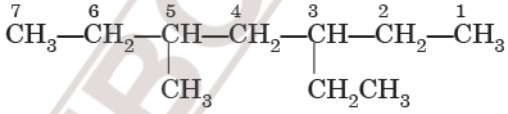
3-Ethyl-2, 2, 3-trimethylhexane

6. Naming different substituents at equivalent positions. *If two different substituents are in equivalent positions from the two ends of the chain (two sets of locants are equally possible), then the numbering of the chain is done in such a way that the group which comes first in the alphabetical order (written first in the name) gets lower number.*

For example, in the compound given below, the methyl and ethyl groups are at equivalent positions.



Methyl at C–3



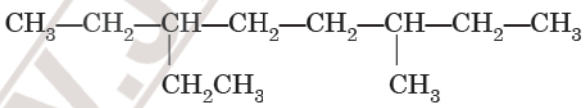
Ethyl at C–3

In such a case, the carbon bearing ethyl group gets lower position because it is cited first in the name according to alphabetical order of substituents. So, correct name of the compound is

3-Ethyl-5-methylheptane

(Not 5-Ethyl-3-methylheptane)

Similarly,

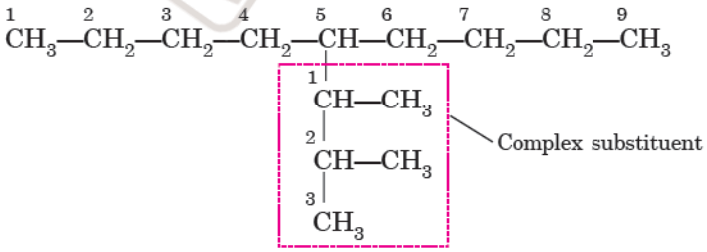


3–Ethyl-6-methyloctane

(Not 3-Methyl-6-ethyloctane)

Some books list the groups in the increasing order of size or complexity (*i.e.*, methyl before ethyl). However, alphabetical order of listing is most widely used.

7. Naming the complex substituents (or substituted substituents). *If the substituent on the parent chain is complex (i.e., it is branched) it is named as substituted alkyl group by numbering the carbon atom of this group attached to the parent chain as 1. The name of such substituent is given in brackets in order to avoid confusion with the numbering of the parent chain.* For example,



5-(1,2-Dimethylpropyl)nonane

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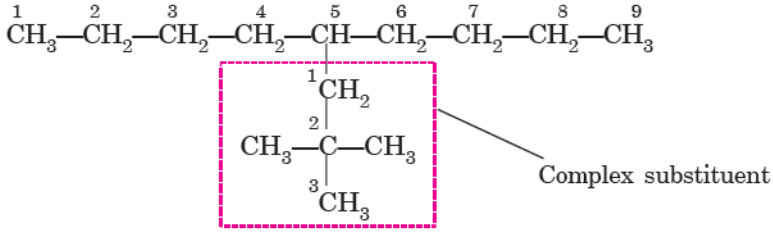
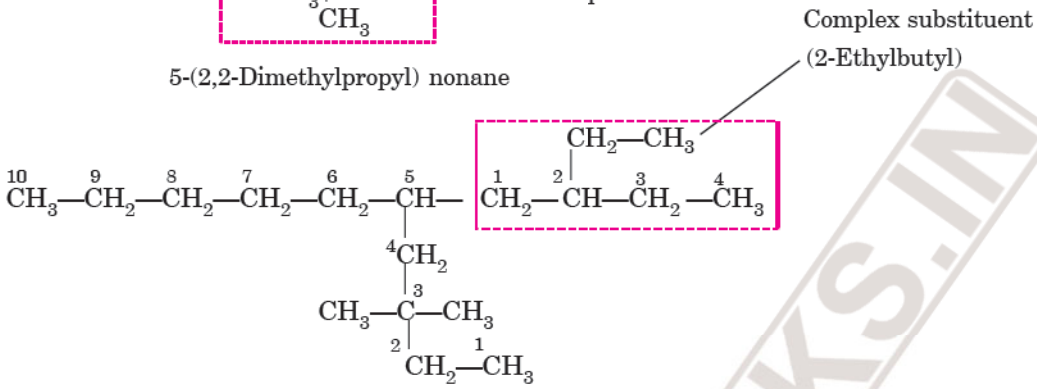


5-(2,2-Dimethylpropyl) nonane



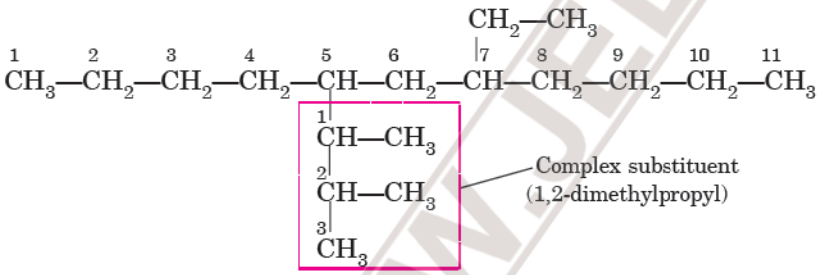
5-(2-Ethylbutyl)-3,3-dimethyldecane

In the complex substituent, the numbering of the carbon atoms is also done. The carbon atom attached to the parent chain is always numbered as 1. So, in the first compound the complex substituent is (1,2-dimethylpropyl).

Some important notes :

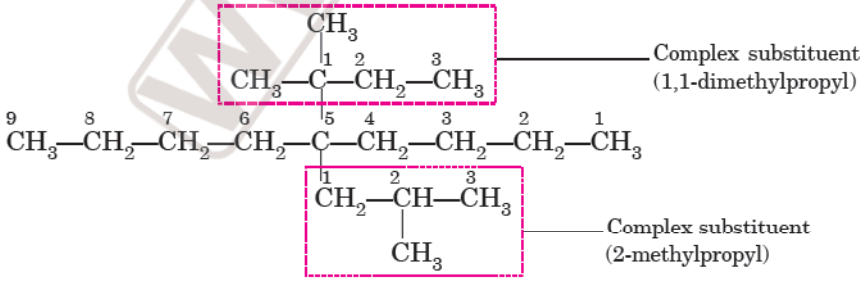
1. *The name of the complex substituent is always written in brackets.*

2. *While deciding the alphabetical order of the various substituents, the name of the complex substituent is considered to begin with the first letter of the complete name.* It may be **remembered** that in case of simple substituents, however, the multiplying prefixes are not considered. The names of simple substituents are first alphabetized and then multiplying prefixes are inserted. For example,



5-(1,2-Dimethylpropyl)-7-ethyl undecane

It may be noted that dimethylpropyl (a complex substituent) is alphabetized under **d** and not under **m**. Therefore, it is cited before ethyl (e).



5-(1,1-Dimethylpropyl) -5-(2-methylpropyl) nonane

The substituent dimethyl is cited first because it is alphabetized under **d**.

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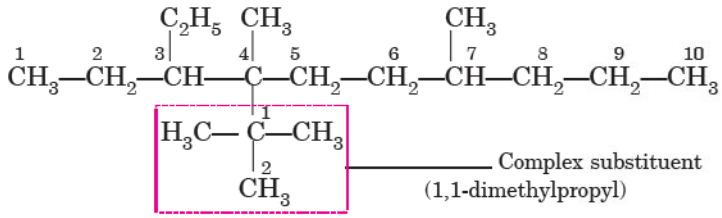
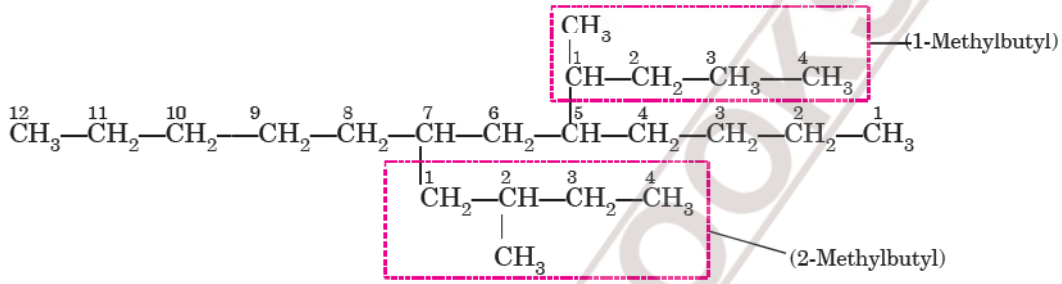
Similarly,



4-(1,1-Dimethylpropyl)-3-ethyl-4,7-dimethyldecane

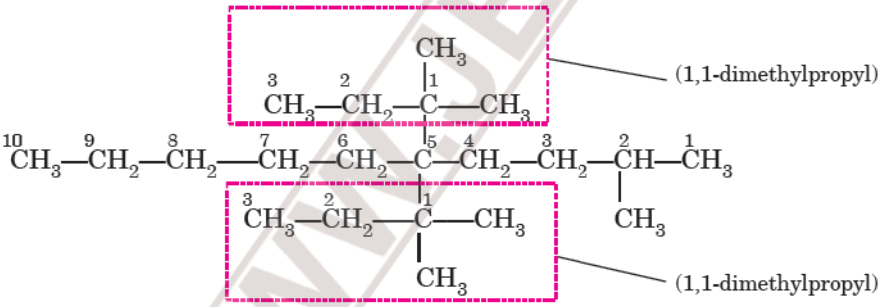
3. *When the names of two or more complex substituents are composed of identical words, priority for citation is given to the substituent which has lowest locant at the first cited point of difference within the complex substituent.* For example,



5-(1-Methylbutyl)-7-(2-methylbutyl) dodecane

The substituent (1-methylbutyl) is written first because it has lower locant than the substituent (2-methylbutyl).

4. When the same complex substituent (substituted in the same way) occurs more than once, it is indicated by the multiplying prefix *bis* (for two), *tris* (for three), *tetra kis* (for four), etc.



5,5-*Bis* (1,1-dimethylpropyl)-2-methyldecane

Bis is used for two same complex substituents.

8. Cyclic or alicyclic hydrocarbons. These compounds contain carbon chain skeletons which are closed to form rings. The saturated hydrocarbons with ring of carbon atoms in the molecule are called *cycloalkanes*. These have the general formula C_nH_{2n}.

The rules for naming these compounds are discussed later (page 47).

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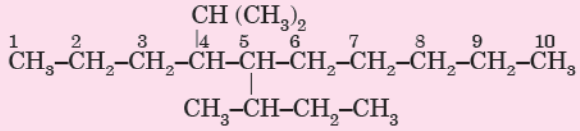
NOTE

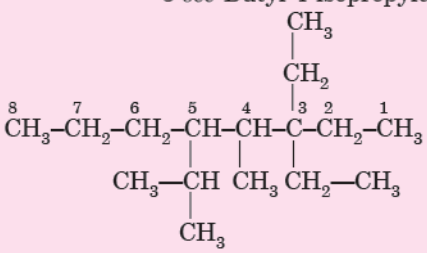
According to the IUPAC system of Nomenclature, certain trivial or semi- systematic names may be used for unsubstituted radicals. For example, the following names may be used :

$(CH_3)_2CH—$	Isopropyl	$(CH_3)_2CH—CH_2—$	*Iso*butyl
$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—$	*sec*-Butyl	$(CH_3)_3C—$	*tert*–Butyl
$(CH_3)_2CH—CH_2—CH_2—$	Isopentyl	$(CH_3)_3C—CH_2–$	Neopentyl
$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}—$	*tert*-Pentyl	$(CH_3)_2CH—CH_2—CH_2—CH–$	Isohexyl

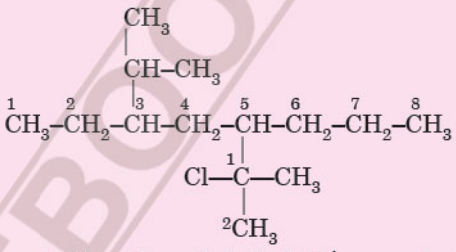
However, when these are substituted, these names cannot be used as such. For example :



5-*sec*-Butyl-4-isopropyldecane



3,3-Diethyl-5-isopropyl-4-methyloctane



5-(1-chloro-1-methylethyl)-3-isopropyloctane

► It may be noted *that while writing the substituent's* name in *alphabetical order,* non-hyphenated prefixes (*iso*,neo) are considered part of the alkyl group for alphabetizing purposes but the hyphenated prefixes (sec-, tert-) are not. For example, isopropyl and isobutyl are listed alphabetically under '*i*', but *sec*- butyl or *tert*-butyl are listed under '*b*'.

Therefore, isopropyl (listed under '*i*') precedes methyl (listed under '*m*') but *tert*-butyl (listed under '*b*') precedes isopropyl (listed under '*i*'). Thus;

- ***di., tri, sec-, tert-* are ignored in alphabetizing.** However, prefixes *sec, tert* are not ignored when they are compared with each other. For example, *sec*-butyl precedes *tert*-butyl.
- ***Iso, neo, cyclo* are not ignored in alphabetizing.**

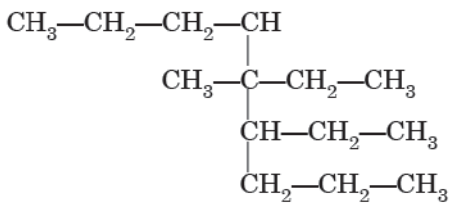
SOLVED EXAMPLES

❑ Example 8.

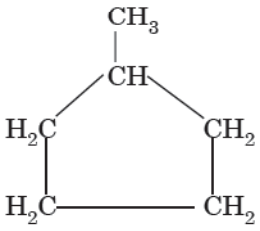
Give IUPAC names for the following hydrocarbons :

(*a*) $CH_3—\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}—\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}—CH_3$

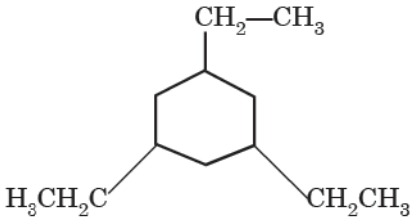
(*b*)



(*c*)



(*d*)



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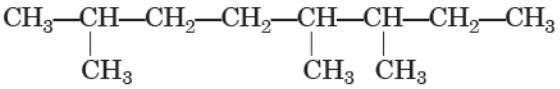
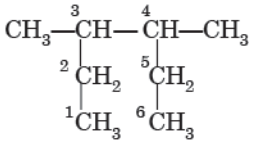
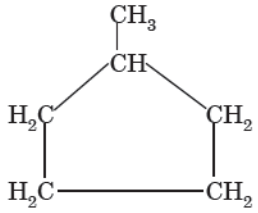
(e) 

Solution : The structure may be written as

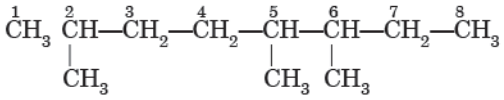
(a) 

The longest chain has 6 carbon atoms and is numbered from lowest left as shown. The two side chains are methyl groups at positions 3 and 4 (from both ends). The name of the compound is **3,4-Dimethylhexane.**

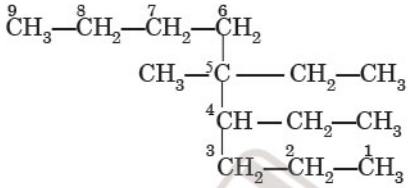
(c) 

Methylcyclopentane

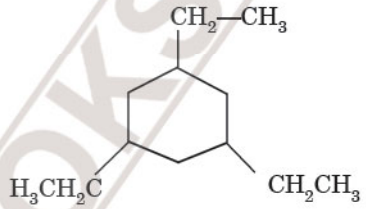
Methyl group is attached to cyclopentane ring. Thus, the name of the molecule is: **Methylcyclopentane**.

(e) 

The longest chain contains 8 carbon atoms. The numbering from left to right gives lowest numbers to the substitutents. The name of the compound is **2,5,6-Trimethyloctane.**

(b) 

The longest chain contains 9 carbon atoms. The chain is numbered from lower right to upper left as shown. The side chains are two ethyl groups at positions 4 and 5 and one methyl group at position 5. The name of the compound is : **4,5-Diethyl-5-methylnonane**

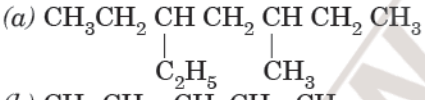
(d) 

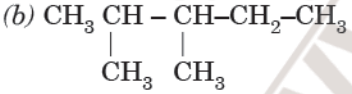
There are three ethyl groups on cyclohexane ring at positions 1, 3 and 5. Thus, the name of molecule is

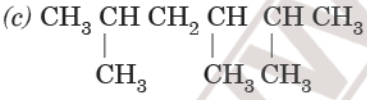
1, 3, 5-Triethylcyclohexane.

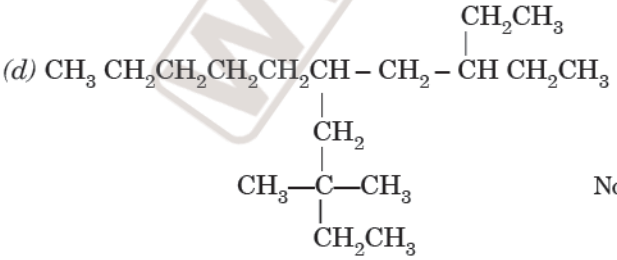
❑ Example 9.

Structures and names of some hydrocarbons are given below. Explain why the names given in parenthesis are not correct :

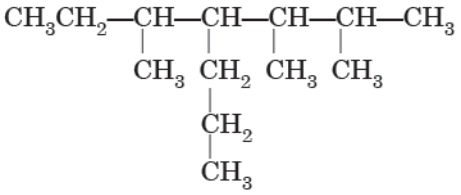
(a)  3- Ethyl-5-methylheptane (Not 5-Ethyl-3-methylheptane)

(b)  2,3–Dimethylpentane (Not 3, 4- Dimethylpentane)

(c)  2,3,5-Trimethylhexane (Not 2,4,5-trimethylhexane)

(d)  5-(2-Ethyl butyl)-3, 3-dimethyldecane

Not 5- (2, 2-dimethyl butyl)-3-ethyldecane

(e)  2,3,5– Trimethyl-4-propylheptane

(Not 4-sec-butyl - 2,3-dimethylheptane)

N.C.E.R.T.

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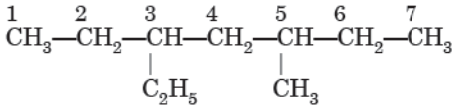
Solution :

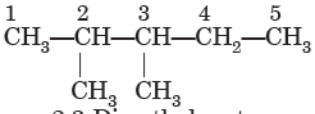
(a)



3-Ethyl-5-methylheptane

Both the substituents ethyl and methyl are in equivalent positions. Lower number is given to the one that comes first in the name according to alphabetical order.

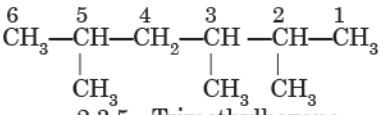
(b)



2,3-Dimethylpentane

Numbering is done from the end which gives lower number to the substituents.

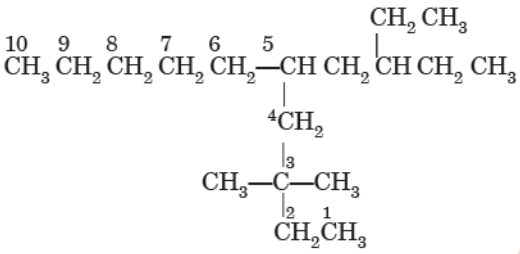
(c)



2,3,5– Trimethylhexane

Lowest locant number 2, 3, 5 is lower than 2, 4, 5.

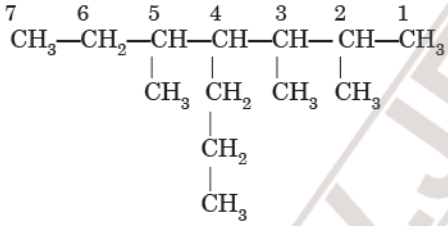
(d)



5-(2- Ethylbutyl) -3, 3-dimethyldecane

Larger number of substituents are attached to the parent chain.

(e)



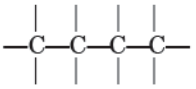
2, 3, 5-Trimethyl-4-propylheptane

Larger number of substituents are attached to the parent chain.

❑ Example 10.

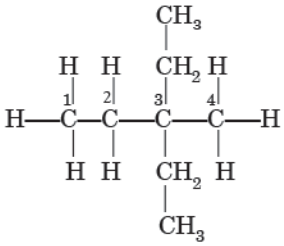
The incorrect IUPAC name of a compound is 3,3-diethyl butane. Write its structural formula and correct the name of the compound.

Solution : 1. As the compound is butane, the parent chain has four carbon atoms :



Parent chain (butane)

2. Number the parent chain from either end. Attach two ethyl substituents at carbon 3 and satisfy the remaining valencies with hydrogen atoms.



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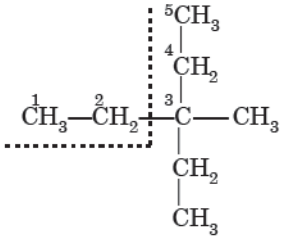
3. In this compound, the longest chain is not of four carbon atoms but of five carbon atoms as shown below :

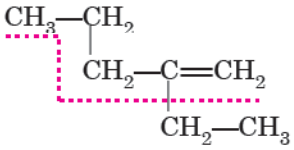


4. Now the correct name of the compound is 3-ethyl-3-methylpentane.

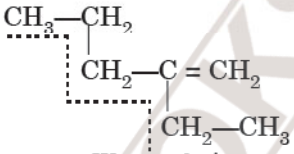
B. Rules for Naming Compounds Containing Double and Triple Bonds

In naming the compounds containing double and triple bonds, the following rules are followed :

1. *Select the longest continuous chain containing the carbon atoms involved in the multiple bonds* ***(double and triple)***. This gives the parent name of the alkene or alkyne. For example, in the structures given below, the longest chain has five carbon atoms.



Correct chain



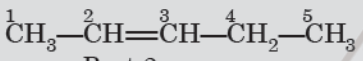
Wrong chain

Note. It may be noted that the selected chain may or may not be the longest chain in the structure. But it must contain double or triple bonded carbon atoms. For example, in the above structure, the longest chain containing double bonded carbon atoms is of five carbon atoms and not of six.

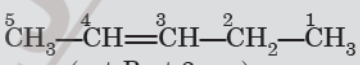
2. *While writing the name of the alkene or alkyne, the suffix 'ane' of the corresponding alkane is replaced by* ***'ene'*** *or* ***'yne'*** *respectively.*

3. *The numbering of atoms in the parent chain is done in such a way that the carbon atom carrying the multiple bonds gets the lowest number.* The position of the multiple bond is then indicated by using the number of the first C-atom of the multiple bond.

Note. It may be noted that we give lowest number to the carbon atom having double or triple bond and not to any side chain (as in alkanes).



Pent-2-ene

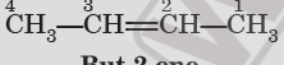


(not Pent-3-ene)

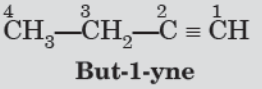
The position of the double bond may be indicated by any of the three ways :

2-Pentene or Pent-2-ene or Pentene-2

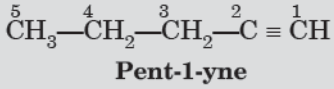
Generally, the first two methods have been in use. However, *according to the latest* **IUPAC convention** *(1993 recommendations), while naming the organic compounds, the locants (numerals and or letters) are placed immediately before the part of the name to which they relate.* This means that in case of unsaturated hydrocarbons the locant of the double bond or triple bond is placed immediately before the suffix **ene** or **yne** and not before the word root as was practice being followed earlier. For example,



But-2-ene
(Formerly 2-Butene)



But-1-yne
(Formerly 1-Butyne)

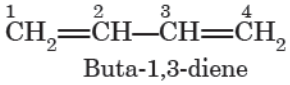


Pent-1-yne
(Formerly 1-Pentyne)

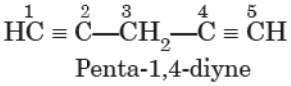
4. *All the rules for naming side chains or substituents are then followed (as in alkanes).*

5. *If the multiple bond occurs two or more times in the chain, then it is named as diene or diyne, triene or triyne,* etc. The position of multiple bonds are also prefixed with numbers.

Some examples are given below :



Buta-1,3-diene



Penta-1,4-diyne

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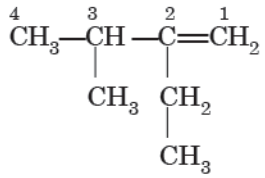
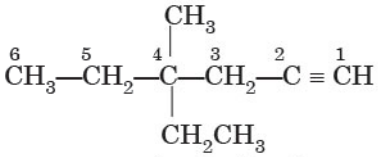
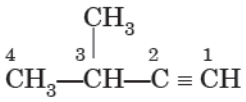


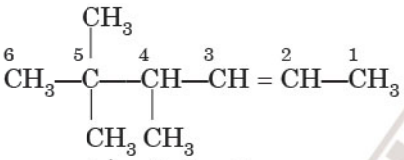
2-Ethyl-3-methylbut-1-ene



4-Ethyl-4-methylhex-1-yne



3-Methylbut-1-yne



4, 5, 5-Trimethylhex-2-ene

IMPORTANT NOTES

If the parent chain contains both the double and triple bonds, the following points should be **kept in mind.**

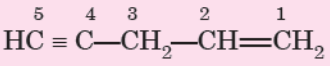
● The terminal *'e'* in the name of alkene is dropped if it is followed by the suffix beginning with *a, i, o, u* or *y*. For example, terminal **e** of the ene is **dropped** in the following cases :

en – **y**ne adien – **y**ne

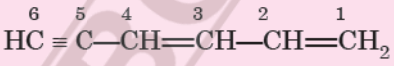
However, terminal **e** is **not dropped** in case of ene –**d**iyne because it comes before d of diyne.

● Numbers as low as possible are given to double bond or triple bond as a set, even though this may at times give *–yne* a lower number than *–ene*. However, if a choice is there, preference for lower locant is given to double bond.

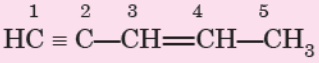
● These compounds are named as derivatives of **alkynes** rather than alkenes. For example



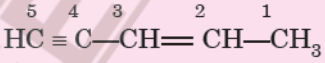
Pent-1-en-4 yne
(Preference of locant for ene)



Hexa-1,3-dien-5-yne

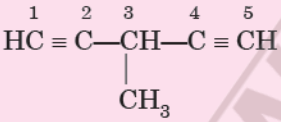


Pent-3-en-1-yne

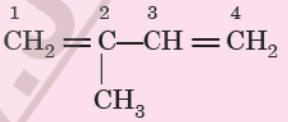


(Not Pent-2-en-4-yne)

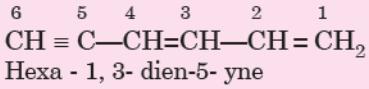
The name of this compound cannot be pent-2-en-4-yne because lowest set is 1, 3 rather than 2, 4.



3-Methylpenta-1,4-diyne



2-Methylbuta-1,3-diene

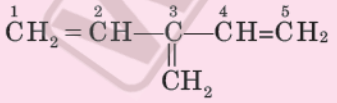


Hexa - 1, 3- dien-5- yne

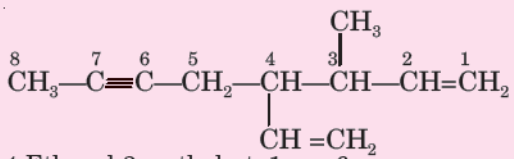
● In some cases, all the double bonds or triple bonds present in the molecule cannot be included in the longest chain. In such cases, the following prefixes are used for double and triple bonded groups acting as substituents.

$CH_2=$	$CH_3CH=$	$CH_2=CH-$	$HC\equiv C-$
Methylene	Ethylidene	Ethenyl or vinyl	Ethynyl

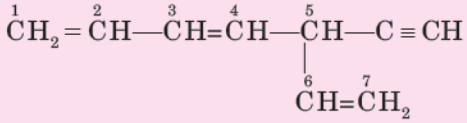
For example,



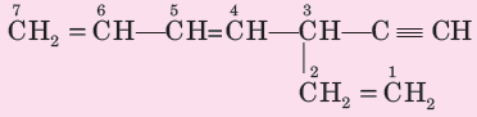
3-Methylenepenta -1, 4-diene



4-Ethenyl-3-methyloct–1–en–6–yne
or 3-Methyl-4-vinyloct-1-en-6-yne



5-Ethynylhepta -1, 3, 6–triene
(Double bond are given preference over the triple bond)



Not: 3-Ethynylhepta-1, 4, 6-triene
(Set of locants are higher)

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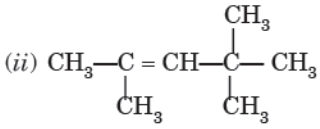
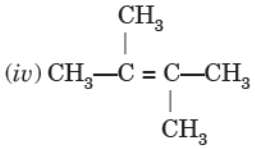
Practice Problems

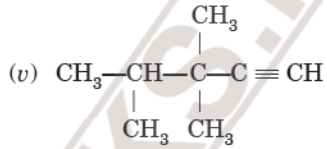
11. Write the structural formulae for :
(*i*) 4-Methyl pent-2-ene (*ii*) 2,2-Dimethylpropane (*iii*) 2-Ethylpent-2-ene
(*iv*) Cyclohexene (*v*) 1,3-Dimethylcyclohexane

12. Give the IUPAC names of :
(*i*) $CH_2 = CHCH = CHCH = CH_2$

(*ii*) 

(*iii*) $(C_2H_5)_2C = C(C_2H_5)_2$

(*iv*) 

(*v*) 

C. Rules for Naming Organic Compounds Containing one Functional Group

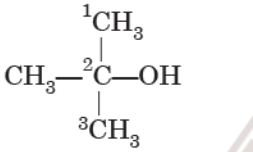
The rules for naming an organic compound are exactly same as discussed already for compounds containing multiple bond. In this case the preference for **lowest number is given to carbon atom containing functional group.** The rules are summarised below :

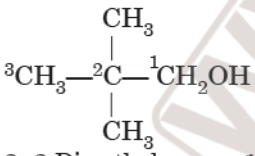
1. *Select the longest continuous chain containing the carbon atom having the functional group without caring whether it also denotes the longest possible carbon chain or not. This is regarded as the parent chain.* This is illustrated below :

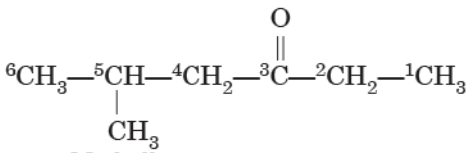
2. *The numbering of atoms in the parent chain is done in such a way that carbon atom bearing the functional group gets the* ***lowest number.***

3. *All the rules for naming side chains or substituents are then followed as discussed in case of alkanes.*

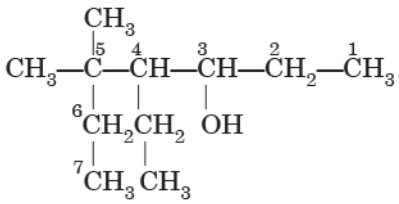
Let us apply these rules to write the names of some compounds.


2-Methylpropan-2-ol


2, 2-Dimethylpropan-1-ol


5-Methylhexan-3-one

It may be noted that the functional group should get the lowest number even if it violates the lowest sum rule.


4-Ethyl-5, 5-dimethylheptan-3-ol

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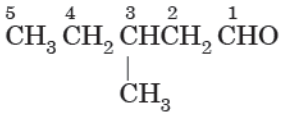
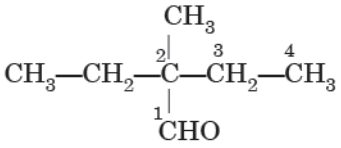


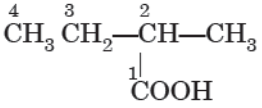
3-Methylpentanal

It may be noted that if a chain terminating functional group such as —CHO, —COOH, —$CONH_2$, — COOR, —CN, etc. is present in the molecule, the numbering of the parent chain in such a case must start from the carbon atom of the functional group. Therefore, **this carbon is always given number 1**. However, this number is normally not indicated in the IUPAC name of the compound.

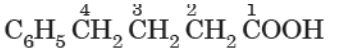
For example,



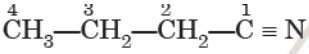
2-Ethyl-2-methylbutanal



2-Methylbutanoic acid

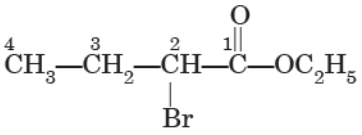


4-Phenylbutanoic acid

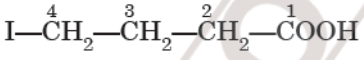


Butane nitrile

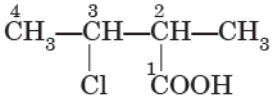
If halogen atom is present in addition to functional group, the halogen is treated as substituent and is written as halo. For example,



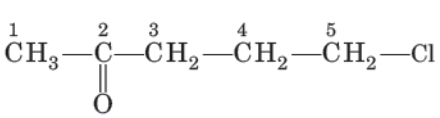
Ethyl 2-bromobutanoate



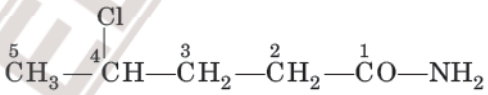
4-Iodobutanoic acid



3–Chloro–2–methylbutanoic acid

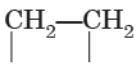


5-Chloropentan-2-one

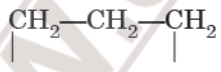


4-Chloropentanamide

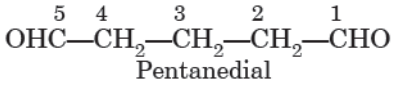
It two or more same functional groups are present, these are indicated by using di (2), tri (3), tetra (4) as prefixes to the name of the functional group.



Ethane-1, 2-diol



Propane-1,3-diol

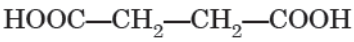


Pentanedial

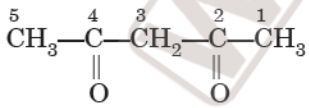
(or Pentane-1, 5-dial)

(No need to give numbers because —CHO is always terminal)

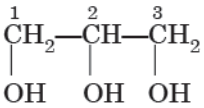
Ethanedioic acid



Butanedioic acid



Pentane-2, 4-dione



Propane-1, 2, 3-triol

LEARNING PLUS

Special note for compounds containing more than two same functional groups

According to latest convention (1993 recommendations for IUPAC nomenclature), if an unbranched chain is directly bonded to more than two same functional groups, the organic compound is named as a derivative of parent alkane which does not include the carbon atoms of the functional groups. These are named by use of suffix such as *tricarboxylic acid* (for three—COOH groups), *tricarbaldehyde* (for three—CHO groups) or *tricarbonitrile* (for three—CN groups).

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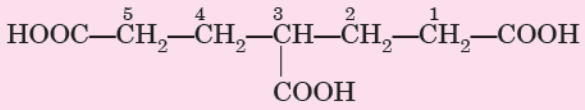
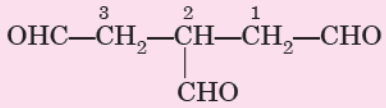
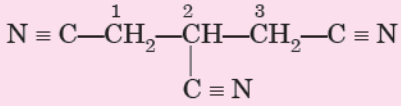
For example,


Pentane-1,3,5-tricarboxylic acid


Propane-1,2,3-tricarbaldehyde

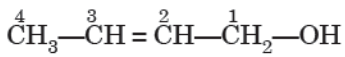

Propane-1,2,3-tricarbonitrile

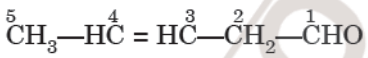
D. Rules for Naming Compounds having functional groups, multiple bonds and side chains/ substituents.

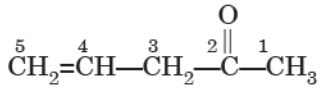
If the organic compound contains a functional group, multiple bond, side chain or the substituent, the following order of preference must be followed :

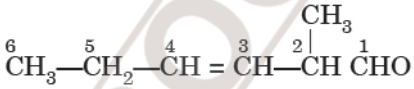
Functional group > Double bond > Triple bond > Side chain

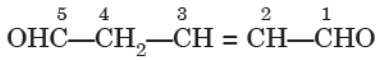
For example,

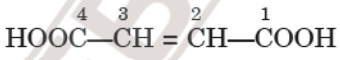

But-2-en-1-ol


Pent-3-en-1-al


Pent-4-en-2-one


2-Methylhex-3-en-1-al

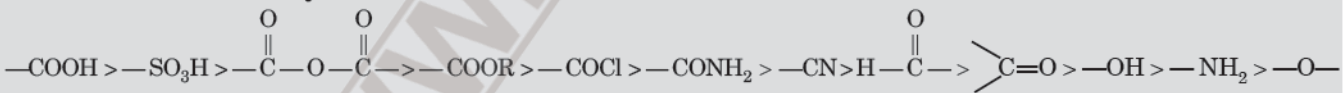

Pent-2-ene-1,5-dial


But-2-ene-1, 4-dioic acid
(or But-2-enedioic acid)

E. Rules for Naming Organic Compounds containing two or more Functional groups

When an organic compound contains two or more functional groups, one group is regarded as the **principal functional group.** The other group is treated as the **secondary functional group** and may be treated as substituent. The following order of priority is used for selecting the principal functional group :

Carboxylic acids > sulphonic acids > acid anhydrides > esters > acid halides > amides > nitriles > aldehydes > ketones > alcohols > amines > ethers



All remaining groups such as halo (fluoro, chloro, bromo, iodo), nitroso (–NO), nitro (– NO_2), alkoxy (–OR), alkyl(R) are treated as substituent groups.

For example, if an organic group contains —COOH and —OH groups, then —COOH group is regarded as the *principal group and* —OH group is the *substituent* and is called hydroxy.

4-Hydroxypentanoic acid

The names of secondary groups which are used as (substituents) prefixes are given below :

Functional group	Prefix	Functional group	Prefix
—COOH	Carboxy	—CHO	Formyl
—COOR	Alkoxy carbonyl or Carbalkoxy	>CO	Oxo or Keto
—COCl	Chloroformyl	—OH	Hydroxy
—$CONH_2$	Carbamoyl	—SH	Mercapto or sulphanyl
—CN	Cyano	—NH_2	Amino
—OR	R-oxy	= NH	Imino
—X	Halo	—NO_2	Nitro

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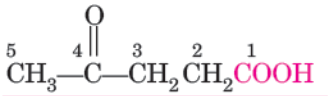
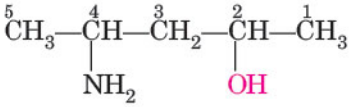
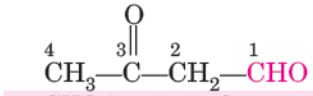
Some examples are :


—COOH is principal group

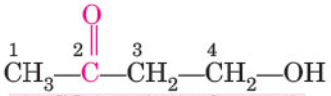
4-Oxopentanoic acid


—OH is principal group

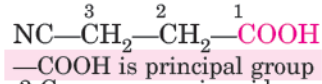
4-Aminopentan-2-ol


—CHO is principal group

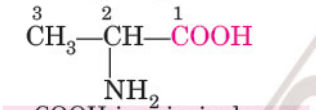
3-Oxobutanal


(—CO is principal group)

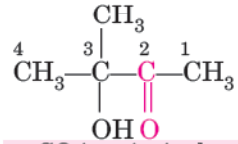
4-Hydroxybutan-2-one


—COOH is principal group

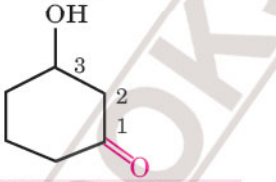
3-Cyanopropanoic acid


—COOH is principal group

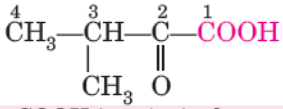
2-Aminopropanoic acid


—CO is principal group

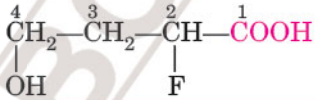
3-Hydroxy-3-methylbutan-2-one


—CO is principal group

3-Hydroxycyclohexanone


—COOH is principal group

3-Methyl-2-oxobutanoic acid

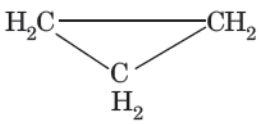

—COOH is principal group

2-Fluoro-4-hydroxybutanoic acid

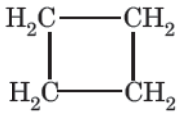
F. Rules for Naming Alicyclic Compounds

The following rules are generally followed for naming alicyclic compounds:

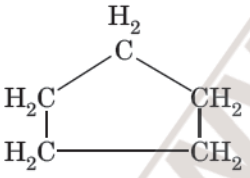
1. *The alicyclic compound is named by prefixing* ***cyclo*** *to the name of the corresponding straight chain hydrocarbon.* For example,


or

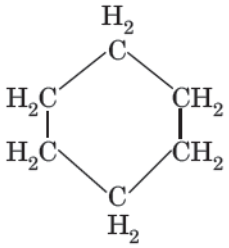
C_3H_6, Cyclopropane


or

C_4H_8, Cyclobutane


or

C_5H_{10} Cyclopentane


or

C_6H_{12} Cyclohexane

For simplicity, the cycloalkanes are also represented by simplified structural formulae without showing C and H atoms as given above. Similarly,

Cyclobutene

Cyclopentene

Cyclohexene

Cyclooctane

Cyclooctene

2. *Substituted alicyclic compounds are named by indicating the name of the substituent before the name of the cycloalkane* as alkyl cycloalkanes, halo cycloalkanes, alkyl cycloalkenes, etc.

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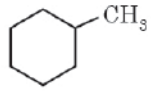
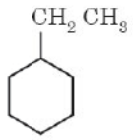
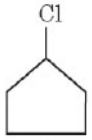
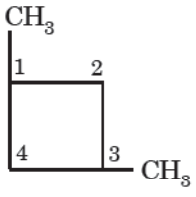
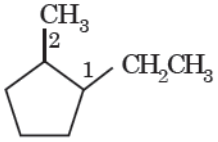

Methylcyclohexane

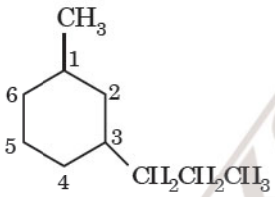

Ethylcyclohexane

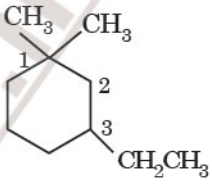

Chlorocyclopentane

3. *If two or more than two alkyl groups or other substituent groups are present in the ring, their positions are indicated by arabic numerals, i.e.,* 1, 2, 3, 4, ... etc. *While numbering the carbon atoms of the ring, the substituent which comes first in the alphabetical order is given the lowest number provided it does not violate the lowest set of locants rule.* For example,

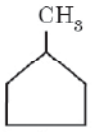

1.3-Dimethylcyclobutane


1-Ethyl-2-methylcyclopentane
(Not 1-Methyl-2-ethylcyclopentane)
[Alphabetical order of numbering]

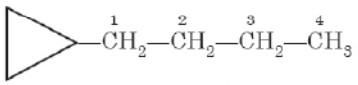

1-Methyl-3-propylcyclohexane
(Not 5-Methyl-1-propylcyclohexane)
[Alphabetical order of numbering]


3-Ethyl-1,1-dimethylcyclohexane
(Not 1-Ethyl-3,3-dimethylcyclohexane)
[More branched chain gets lower number]

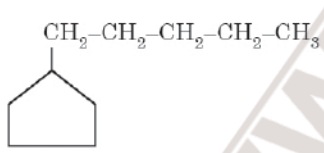
4. (*a*) *If the number of carbon atoms in the ring is equal to or more than the number of carbon atoms in the alkyl group attached to it (or substituent) then it is named as an alkyl substituted cycloalkane. But if the number of carbon atoms in the largest substituent is greater than the number of carbon atoms in the ring then it is named as cycloalkyl substituted alkane.*

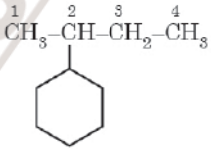

Methylcyclopentane
(Chain of 1 C atom, ring of 5 C atoms)

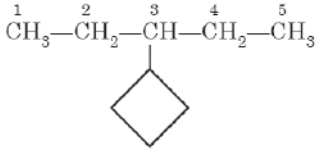
But

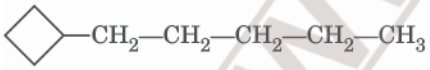

1-cyclopropylbutane
(Chain of 4 C atoms, ring of 3 C atoms)

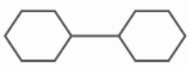
For example,

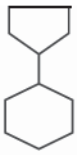

Pentylcyclopentane

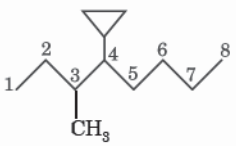

(2-Butyl) cyclohexane
or (1-Methylpropyl)cyclohexane

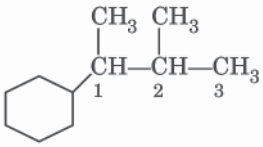

3-Cyclobutylpentane

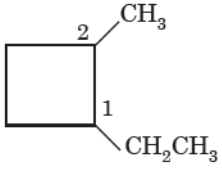

1-Cyclobutylpentane


Cyclohexyl cyclohexane


Cyclopentyl cyclohexane


4-Cyclopropyl-3-methyloctane


(1,2-dimethylpropyl) cyclohexane


1-Ethyl-2-methylcyclobutane

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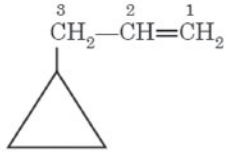
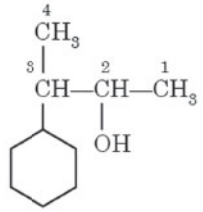
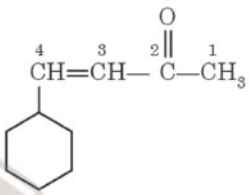
(b) If the side chain contains a multiple bond or a functional group the alicyclic ring is treated as the substituent irrespective of the size of the ring. For example,



3-Cyclopropylprop-1-ene

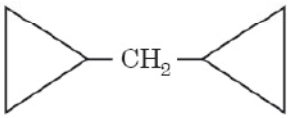


3-Cyclohexylbutan-2-ol

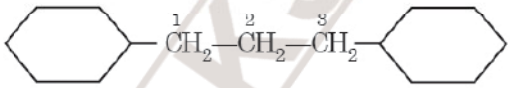


4-Cyclohexylbut-3-en-2-one

(c) If more than one alicyclic ring is attached to a single chain, the compound is named as a derivative of alkane irrespective of the number of carbon atoms in the ring or the chain. For example.

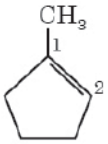


Dicyclopropylmethane

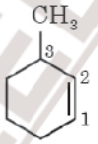


1, 3- Dicyclohexylpropane

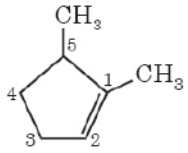
5. *If a multiple (double or triple) bond and some other substituents are present in the ring, the numbering is done in such a way that the carbon atoms of the multiple bond get lowest locants 1 and 2 and the substituent groups get the lower locants at the first point of difference. For example,*



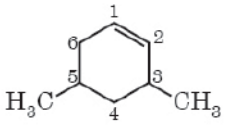
1-Methylcyclopent-1-ene



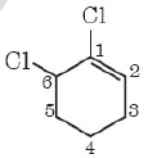
3-Methylcyclohex-1-ene



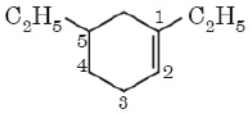
1,5 Dimethylcyclopent-1-ene
(Not 2, 3-Dimethylcyclopent-1-ene)



3, 5-Dimethylcyclohex-1-ene
(Not 4, 6-Dimethylcyclohex-1-ene)

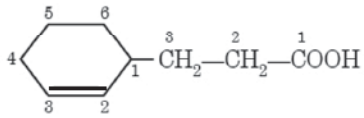


1,6-Dichlorocyclohex-1-ene

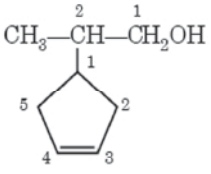


1,5-Diethylcyclohex-1-ene
(Not 2, 4-Diethylcyclohex-1-ene)

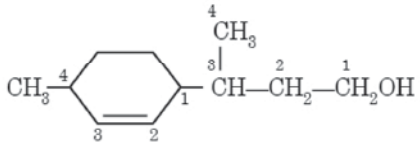
6. *If the side chain contains a functional group and the ring contains a multiple bond, then the ring is treated as a substituent and the compound is named as derivative of the alkyl chain.*



3-(Cyclohex-2-enyl)propanoic acid



2-(Cyclopent-3-enyl)propan-1-od



3- (4-Methylcyclohex-2-enyl)butan-1-ol

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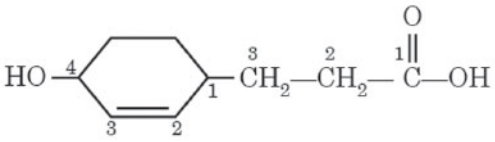
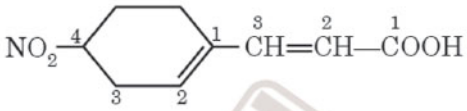
7. *If the ring as well as the side chain contain functional groups, the compound is named as a derivative of the alicyclic ring or the side chain depending upon whether the ring or the side chain contains the principal functional group.*

For example,



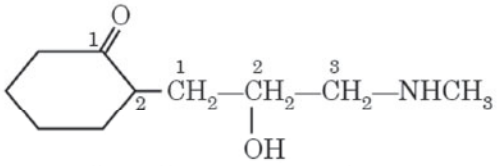
3-(4-Hydroxycyclohex-2-enyl) propanoic acid

—COOH is principal group



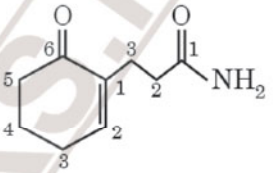
3-(4-Nitrocyclohex-1-enyl) prop-2-en-1-oic acid

—COOH is principal group



2-(3-Aminomethyl-2-hydroxypropyl) cyclohexan-1-one

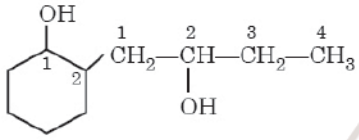
—CO group is principal group



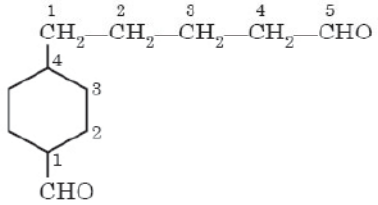
3-(6-Oxocyclohex-1-enyl) propanamide

—$CONH_2$ is principal group

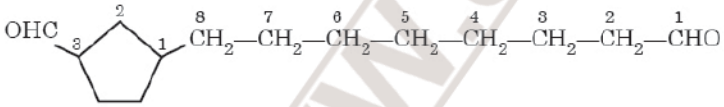
However, if the alicyclic ring and the side chain contains the same functional group, the compound is named as a derivative of side chain or ring according as the side chain or the ring contain larger number of carbon atoms. For example,



2-(2-Hydroxybutyl) cyclohexan-1-ol

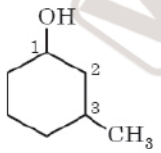


4-(5-Formylpentyl) cyclohexane-1-carbaldehyde

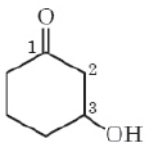


7-(3-Formylcyclopentyl) octanal

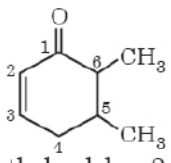
8. *If some functional group along with other substituent group are present in the ring, it is indicated by some appropriate prefix or suffix and its position is indicated by numbering the carbon atoms of the ring in such a way that the functional group gets the lowest locant. For example,*



3-Methylcyclohexan-1-ol



3-Hydroxycyclohexan-1-one



5,6-Dimethylcyclohex-2-en-1-one

9. *If an alicyclic ring is directly attached to a carbon containing functional group, the carbon of the functional group is not included in the parent name of the alicyclic system. In these systems, the prefixes and suffixes for the functional groups are commonly used.*

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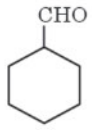
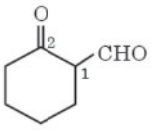
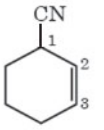


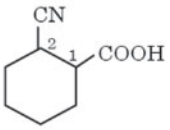
Cyclohexane carbaldehyde



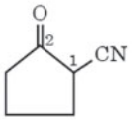
2-Oxocyclohexane-1-carbaldehyde



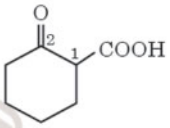
Cyclohex-2-ene-1-carbonitrile



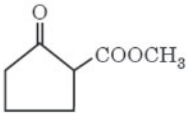
2-Cyanocyclohexane-1-carboxylic acid



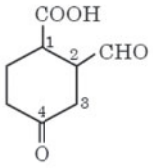
2-Oxocyclopentane-1-carbonitrile



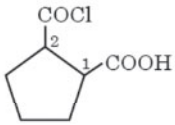
2-Oxocyclohexane-1-carboxylic acid



Methyl (2-oxocyclopentane)-1-carboxylate

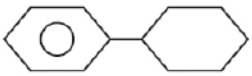


2-Formyl-4-oxocyclohexane-1-carboxylic acid

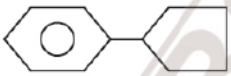


2-Chlorocarbonylcyclohexane-1-carboxylic acid

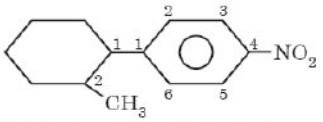
If the alicyclic ring is directly linked to benzene ring (discussed later), it is treated as cycloalkyl substituent irrespective of the number of carbon atoms in the ring. Therefore, it is named as derivative of benzene. For example,



Cyclohexyl benzene



Cyclopentyl benzene



1-(2-Methylcyclohexyl)-4-nitrobenzene

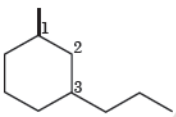
Bond Line Notation

Sometimes, the bonds between carbon atoms are represented by lines. For example, *n*-hexane has a continuous chain of six carbon atoms which may be represented as :

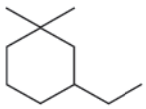
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

n-Hexane

In this notation, the carbon atoms are represented by line ends and intersections. It is assumed that the required number of hydrogen atoms are present wherever they are necessary to satisfy the tetravalency of carbon. A single line represents a single bond (C—C), two parallel lines represent a double bond (C=C) and three parallel lines represent a triple bond (C ≡ C). For example,

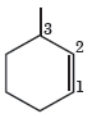


1- Methyl-3-propylcyclohexane



3-Ethyl-1,1-dimethylcyclohexane

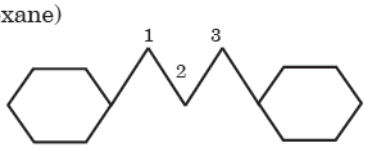
(Not 1-ethyl-3, 3-dimethylcyclohexane)



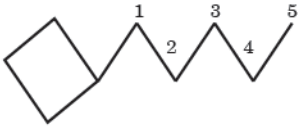
3-Methylcyclohex-1-ene

Pent-1-ene

Buta-1,3-diene

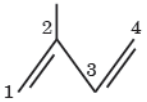


1,3-Dicyclohexylpropane



1-Cyclobutylpentane

Penta-1,4-diene



2-Methylbuta-1, 3-diene

(a line at position 2 corresponds to CH_3 group)

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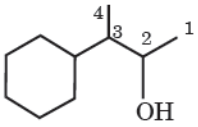
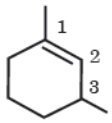
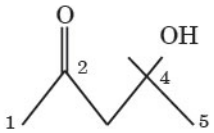


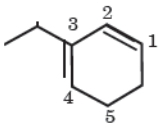
3-Cyclohexylbutan-2-ol



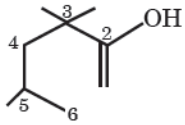
1,3-Dimethyl cyclohex-1-ene



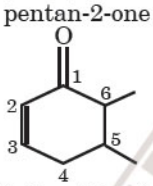
4-Hydroxy-4-methyl pentan-2-one



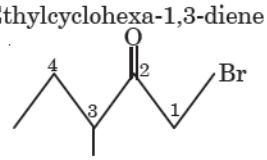
3-Ethylcyclohexa-1,3-diene



3,3,5-Trimethylhex-1-en-2-ol



5,6-Dimethylcyclohex-2-en-1-one



1-Bromo-3-methylpentan-2-one

Hexa-1,3,5-triene

WRITING STRUCTURAL FORMULA FROM THE NAME OF THE COMPOUNDS

We have discussed how to write the name of an organic compound, if its structure is given. Now let us do the reverse *i.e.,* to write the structure of an organic compound if its name is given. For this purpose, the procedure is as follows :

(i) Write a straight chain of carbon atoms according to the number of carbon atoms in the parent compound. At this stage, do not attach any hydrogen atoms to complete the tetravalency of carbon as

C—C—C—C—C—C

(ii) Number the chain of carbon atoms from any end

$\overset{1}{C}—\overset{2}{C}—\overset{3}{C}—\overset{4}{C}—\overset{5}{C}—\overset{6}{C}$

(iii) In case, the name of the compound contains -ene or -yne, then fill double or triple bond at indicated positions.

For example, 2-ene may be indicated as

$\overset{1}{C}—\overset{2}{C}=\overset{3}{C}—\overset{4}{C}—\overset{5}{C}—\overset{6}{C}$

(iv) Attach substituents and functional groups at the desired positions.

(v) Make each carbon tetravalent by attaching a suitable number of hydrogen atoms.

Let us illustrate the above procedure by the following examples.

SOLVED EXAMPLES

❑ Example 11.

Write the structural formulae of the following compounds :

(a) But-2-en-1-oic acid

(b) 2, 4, 4-Trimethyl-3-isopropylpent-1-ene.

Solution : *(a) But-2-en-1-oic acid*

(i) The word root *but* indicates that the compound has four C atoms.

C—C—C—C

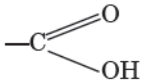
(ii) Let us number each carbon atom of the chain as :

$\overset{1}{C}—\overset{2}{C}—\overset{3}{C}—\overset{4}{C}$

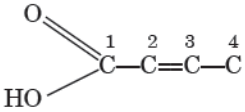
(iii) Since its name has 2-en, it means double bond starts from carbon atom no. 2.

$\overset{1}{C}—\overset{2}{C}=\overset{3}{C}—\overset{4}{C}$

(iv) Since the name of the compound ends in 1-oic acid, hence the first carbon atom will have



group as:



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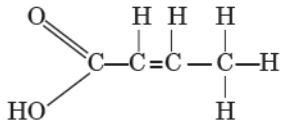
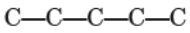
(*v*) Attach suitable number of hydrogen atoms.



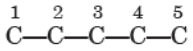
or $CH_3CH = CHCOOH$

(*b*) *2, 4, 4-Trimethyl-3-isopropyl pent-1-ene*

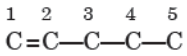
(*i*) As the name of the compound has the word root pent, it has five carbon atoms.



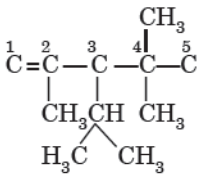
(*ii*) Let us number each carbon atom of the chain



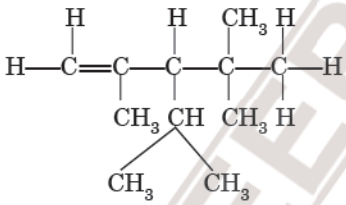
(*iii*) Since its name has 1-ene, it means that double bond starts from first carbon atom.



(*iv*) Attach three methyl radicals at 2, 4 and 4 positions and one isopropyl radical at 3 position.



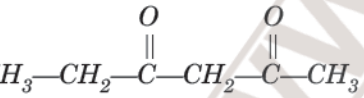
(*v*) Attach suitable number of hydrogen atoms.

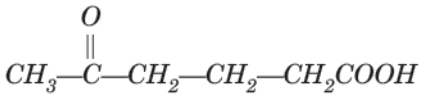


❑ Example 12.

Write the IUPAC names of the following compounds :

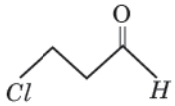
(*i*) $CH_3\,CH_2\,CH\,CH_2\,CH_2\,CH\,CH_2\,CH_3$ (OH, CH_3)

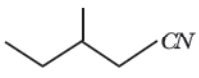
(*ii*) 

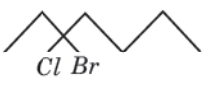
(*iii*) 

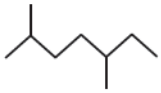
(*iv*) $HC \equiv C - CH = CH - CH = CH_2$

(*v*)

(*vi*) 

(*vii*) 

(*viii*) 

(*ix*) 

(*x*) $Cl_2\,CH\,CH_2OH$

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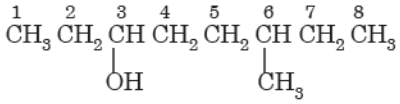
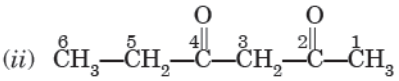
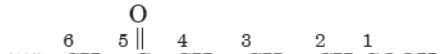
Solution :

(*i*) 

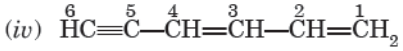
6-Methyloctan-3-ol

(*ii*) 

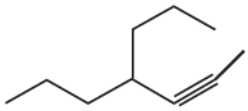
Hexane-2, 4-dione

(*iii*) 

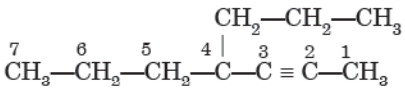
5-Oxohexanoic acid

(*iv*) 

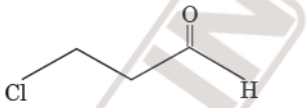
Hexa-1,3-dien-5-yne

(*v*) 

or

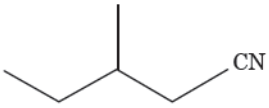


4-Propylhept-2-yne

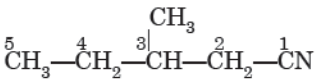
(*vi*) 

or

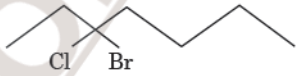
3-Chloropropanal

(*vii*) 

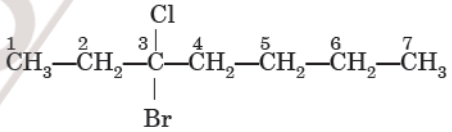
or



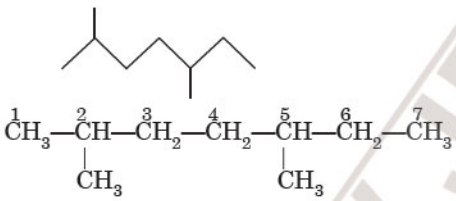
3-Methylpentanenitrile

(*viii*) 

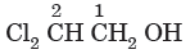
or



3-Bromo-3-chloroheptane

(*ix*) 

2,5-Dimethylheptane

(*x*) 

2,2-Dichloroethanol

❑ Example 13

Which of the following represent the correct IUPAC name for the compounds concerned :

(i) But -3-yn-1-ol or But-4-ol-1-yne

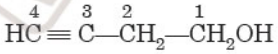
(ii) 4-Chloro-2-methylpentane or 2-Chloro-4-methylpentane

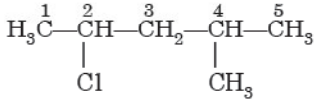
(iii) 2, 2,-Dimethylpentane or 2-Dimethylpentane

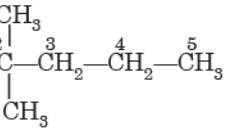
(iv) 2, 3- Dimethylpentane or 3, 4,-Dimethylpentane

(v) 2, 4, 7- Trimethyloctane or 2, 5, 7-Trimethyloctane.

Solution :

(*i*) But-3-yn-1-ol :  Functional group (–OH) gets preference in numbering the carbon chain.

(*ii*) 2-Chloro–4–methylpentane :  Chloro substituent gets preference in numbering.

(*iii*) 2, 2 -Dimethylpentane :  Position of both the substituents are indicated separately.

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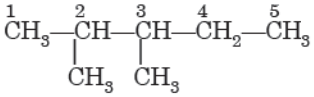
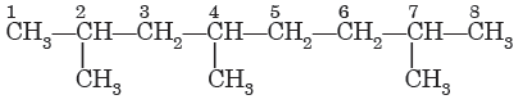
(*iv*) 2, 3-Dimethylpentane :  It has lowest set of locants.

(*v*) 2, 4, 7-Trimethyloctane :  It has lowest set of locants.

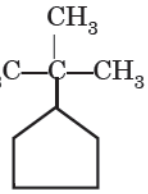
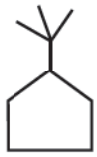
❑ **Example 14.**

Write bond line formula for

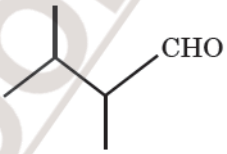
(i) tert-Butylcyclopentane *(ii) Isopropylalcohol*

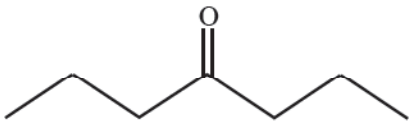
(iii) 2, 3-Dimethylbutanal *(iv) Heptan-4-one*

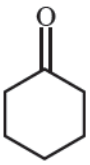
(v) Cyclohexanone

Solution : (*i*)  or 

(*ii*)

(*iii*) 

(*iv*) 

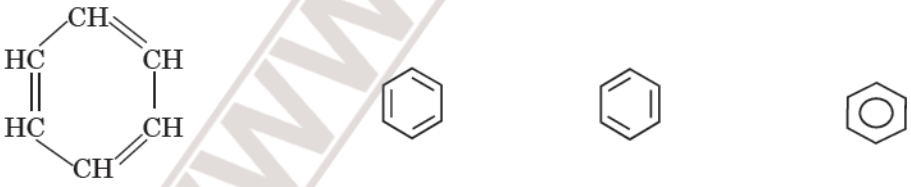
(*v*) 

NOMENCLATURE OF SIMPLE AROMATIC COMPOUNDS

Aromatic compounds are those which contain one or more benzene rings in them. An aromatic compound has two main parts :

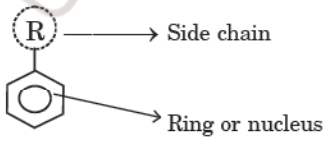
(*i*) Nucleus (*ii*) Side chain

(*i*) **Nucleus.** *The benzene ring represented by regular hexagon of six carbon atoms with three double bonds in the alternate positions is referred to as* **nucleus.** The ring may be represented by any of the following ways :



(*i*) (*ii*) (*iii*) (*iv*)

(*ii*) **Side chain.** *The alkyl or any other aliphatic group containing at least one carbon atom attached to the nucleus* is called **side chain**. These are formed by replacing one or more hydrogen atoms in the ring by alkyl radicals *i.e.,* R(R may be —CH_3, —C_2H_5, —C_3H_7 etc.)



If one atom of hydrogen of benzene molecule is replaced by another atom or group of atoms, the derivative formed is called **monovalent substituted derivative**. It can exist only in one form because all the six hydrogens of benzene represent equivalent positions. For example, C_6H_5X, where X is a monovalent group.

When two hydrogen atoms of benzene are replaced by two monovalent atoms or group of atoms, the resulting product can have three different forms. These forms are distinguished by giving the numbers. The

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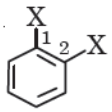
position occupied by one of the substituent is given as 1 and the other position is numbered in a clockwise direction.

(i) **Ortho (or 1, 2-).** The compound is said to be ortho (or 1,2-) if the two substituents are on the adjacent carbon atoms.

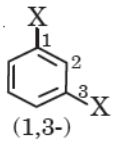
(ii) **Meta (or 1, 3-).** The compound is said to be meta or (1,3-) if the two substituents are on alternate carbon atoms.

(iii) **Para (or 1, 4-).** The compound is said to be para (or 1,4-) if the two substituents are on diagonally situated carbon atoms.

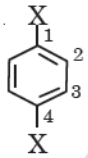
Ortho, meta and para are generally represented as *o*-, *m*- and *p*- respectively as shown below :



(1,2-)
Ortho



(1,3-)
Meta

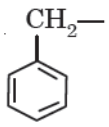


(1,4)
Para

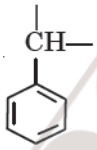
Aryl group. *The radicals obtained by removal of one or more hydrogen atoms of the aromatic hydrocarbon molecules* are known as *aryl radicals or aryl groups*. For example,

Phenyl *o*-tolyl

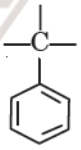
From nucleus



Benzyl



Benzal



Benzo

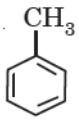
From side chains

Nomenclature of Different Aromatic Compounds

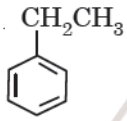
The names of few simple aromatic compounds are given below :

Hydrocarbons

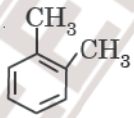
Benzene



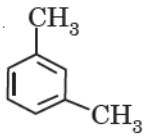
Methylbenzene
(Toluene)



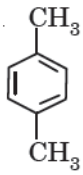
Ethylbenzene



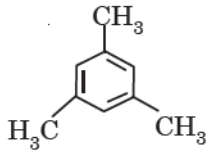
1,2-Dimethylbenzene
(*o*-xylene)



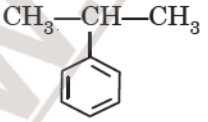
1,3-Dimethylbenzene
(*m*-Xylene)



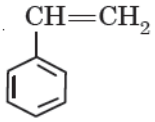
1, 4-Dimethylbenzene
(*p*-Xylene)



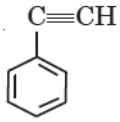
1, 3, 5-Trimethylbenzene
(Mesitylene)



(2-Propyl) benzene
(Isopropyl benzene
or Cumene)

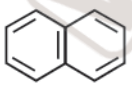


Ethenylbenzene
(Styrene)

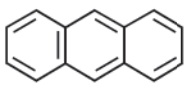


Ethynylbenzene
(Phenylacetylene)

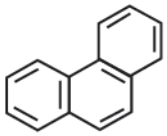
The aromatic hydrocarbons may also contain two or more benzene rings condensed together.



Naphthalene



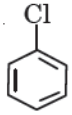
Anthracene



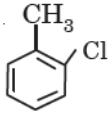
Phenanthrene

Halogen derivatives

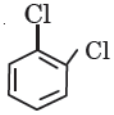
Nuclear substituted



Chlorobenzene



2-Chlorotoluene
(*o*-Chlorotoluene)



1,2-Dichlorobenzene
(*o*-Dichlorobenzene)

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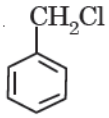
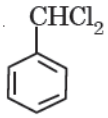
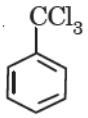
Side chain substituted


Phenylchloromethane
(Benzyl chloride)

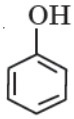

Phenyldichloromethane
(Benzal chloride)

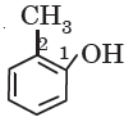

Phenyltrichloromethane
(Benzo chloride)

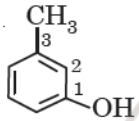
Hydroxy derivatives

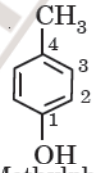
The nuclear hydroxy derivatives are called **phenols** while the side chain substituted hydroxy derivatives are called **aromatic alcohols.**

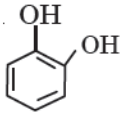
(*i*) Phenols

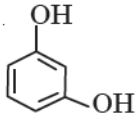

Phenol

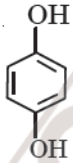

2-Methylphenol
(*o*-Cresol)

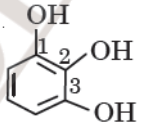

3-Methylphenol
(*m*-Cresol)

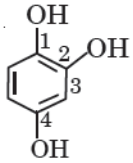

4-Methylphenol
(*p*-Cresol)


1,2-Dihydroxybenzene
(Catechol)

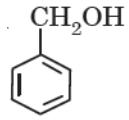

1, 3-Dihydroxybenzene
(Resorcinol)

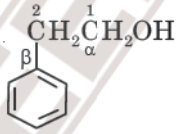

1, 4-Dihydroxy-
-benzene
(Hydroquinone
or Quinol)

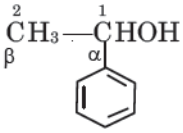

Benzene-1, 2, 3-triol
(Pyrogallol)


Benzene-1, 2, 4-triol
(Hydroquinol)

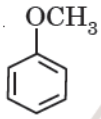
(*ii*) Aromatic alcohols

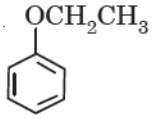

Phenylmethanol
(Benzyl alcohol)

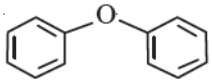

2-Phenylethanol
(β-Phenyl ethyl alcohol)


1-Phenylethanol
(α-Phenyl ethyl alcohol)

Ethers

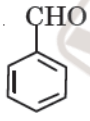

Methoxybenzene
(Anisole or Methyl phenyl ether)

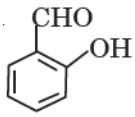

Ethoxybenzene
(Phenetole or Ethyl phenyl ether)

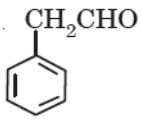

Phenoxybenzene
(Diphenyl ether)

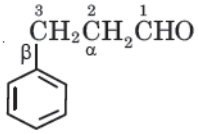
Aldehydes and ketones

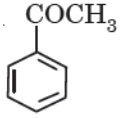
Nuclear substituted

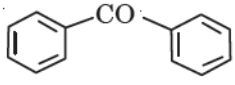

Benzaldehyde

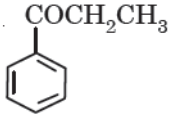

2-Hydroxy benzaldehyde
(Salicylaldehyde)

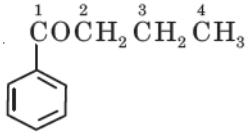

2-Phenylethanal
(Phenyl acetaldehyde)


3-Phenylpropanal
(β-Phenylpropionaldehyde)


1-Phenylethan-1-one
(Methyl phenyl ketone
or acetophenone)


Diphenyl ketone
(Benzophenone)
or diphenyl ketone


1-Phenylpropan-1-one
(Propiophenone
or ethylphenyl ketone)


1-Phenylbutan-1-one
(Butyrophenone or
Phenyl-n-propylketone)

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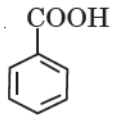
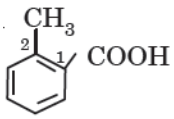
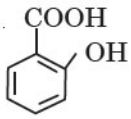
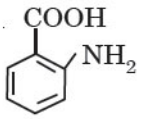
Carboxylic acids

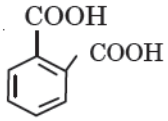
Nuclear substituted

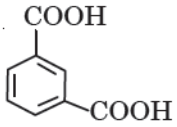

Benzoic acid

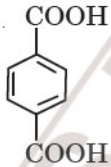

2-Methylbenzoic acid
(*o*-Toluic acid
or *o*-methyl benzoic acid)


2-Hydroxybenzoic acid
(*o*-Salicylic acid or *o*-Hydroxy
benzoic acid)

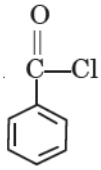

2-Aminobenzoic acid
(Anthranilic acid or
o-Aminobenzoic acid)

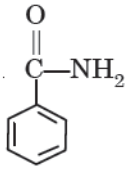

Benzene-1, 2-dicarboxylic
acid
(Phthalic acid)

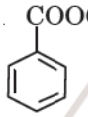

Benzene-1, 3-dicarboxylic acid
(Isophthalic acid)

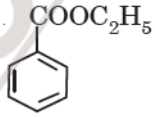

Benzene-1,4-dicarboxylic
acid
(Terephthalic acid)

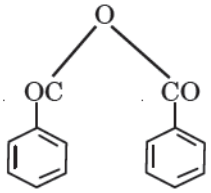
Acid derivatives

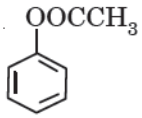

Benzenecarbonyl chloride
(Benzoyl chloride)

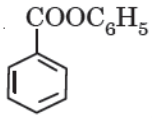

Benzamide

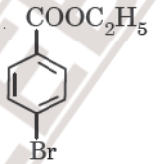

Methyl benzoate

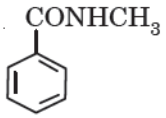

Ethyl benzoate

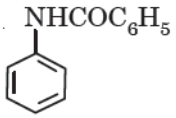

Benzoic anhydride


Phenyl ethanoate
(Phenyl acetate)


Phenyl
benzoate

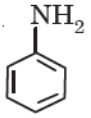

Br
Ethyl 4-bromobenzoate

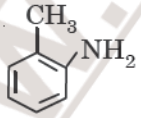

N-Methylbenzamide

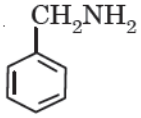

N-Phenylbenzamide
(Benzanilide)

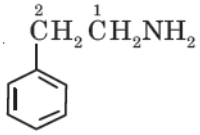
Amino derivatives

Nuclear substituted

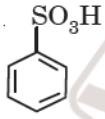

Aniline or benzenamine
(Aminobenzene)

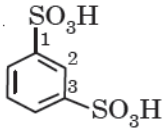

2-Aminotoluene
(*o*-Toluidine)

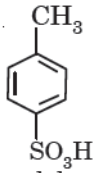

Phenylmethanamine
(Benzyl amine)


2-Phenylethanamine
(β-Phenyl ethylamine)

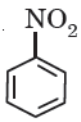
Sulphonic acids

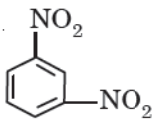

Benzenesulphonic acid

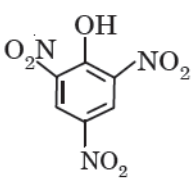

Benzene-1, 3-disulphonic acid
(*m*-Benzene disulphonic acid)


4-Toluenesulphonic acid
(*p*-Toluene sulphonic acid)

Nitro derivatives


Nitrobenzene


1, 3-Dinitrobenzene
(*m*-Dinitrobenzene)


2, 4, 6-Trinitrophenol
(Picric acid)

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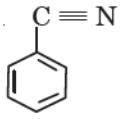
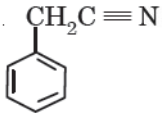
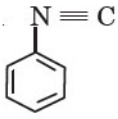
Cyanides and isocyanides



Benzene carbonirile (Benzonitrile or Phenyl cyanide)



Phenylethanenitrile (Benzyl cyanide or Phenyl acetonitrile)



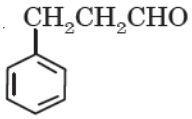
Phenylisocyanide or Phenyl carbylamine

SOME TIPS FOR NOMENCLATURE OF AROMATIC COMPOUNDS

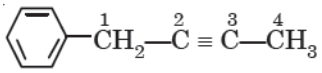
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as *prefix* to the word benzene. It may be noted that common names of many substituted benzene compounds are still universally used. Some important tips for nomenclature of organic compounds are given below :

1. When the benzene ring is named as substituent on the other molecule, it is named as **phenyl group.** It is treated in the nomenclature just like the name of an alkyl group. It is abbreviated as Ph.

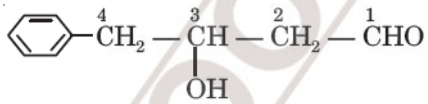
For example,



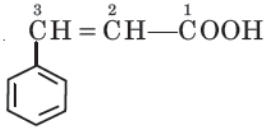
or Ph CH_2CH_2CHO 3-Phenylpropanal



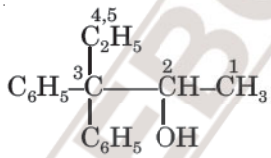
1-Phenylbut-2-yne



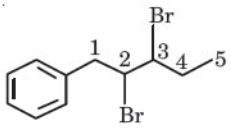
4-Phenyl-3-hydroxybutanal



3-Phenylprop-2-enoic acid

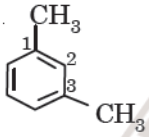


3, 3-Diphenyl pentan-2-ol

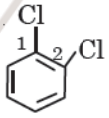


2, 3-Dibromo-1-phenylpentane

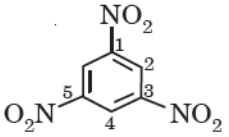
2. Disubstituted, trisubstituted or tetrasubstituted benzenes are named by using the numbers for the positions of the substituents.



1,3-Dimethylbenzene



1,2-Dichlorobenzene



1,3,5-Trinitrobenzene

3. If different groups are attached to the benzene ring, then the following rules are **kept in mind :**

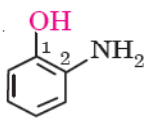
(*i*) When an aromatic compound contains two or more functional groups, it is named as a derivative of the compound with the principal group fixed as number 1.

(*ii*) The numbering of the chain is done in any direction (clockwise or anticlockwise) which gives lower number to the substituent.

(*iii*) The substituents are written in alphabetical order.

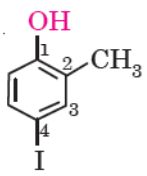
For example,

- Fixing the position of principal group as number 1.



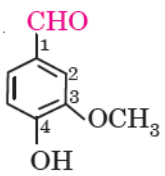
2-Aminophenol

–OH group is principal group



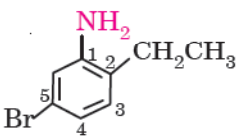
4-Iodo-2-methylphenol

–OH group is principal group



4-Hydroxy-3-methoxy benzaldehyde

–CHO group is principal group



5-Bromo-2-ethylaniline

–NH_2 group is principal group

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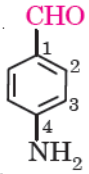
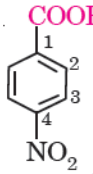
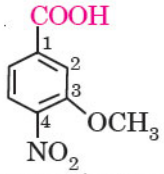

4-Aminobenzaldehyde

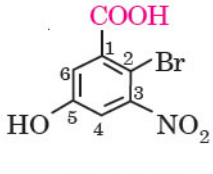
–CHO is principal group


4-Nitrobenzoic acid

–COOH is principal group

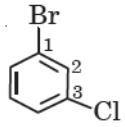

3-Methoxy-4-nitrobenzoic acid

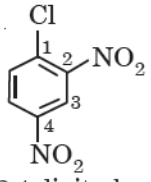
–COOH is principal group

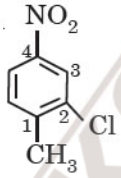

2-Bromo-5-hydroxy-3-nitrobenzoic acid

–COOH is principal group

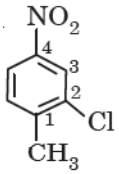
- If all the groups present in the benzene ring are different and none of these gives a special name to the molecule, then these groups are arranged in alphabetical order. The group named first in the alphabetical order gets the lowest number provided it does not violate the lowest locant rule for all the substituents. The name of the molecule ends with the word **benzene.**

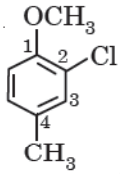

1-Bromo-3-chlorobenzene (**Not:** 1-Chloro-3-bromobenzene)

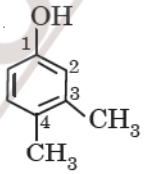

1-Chloro-2,4-dinitrobenzene (**Not:** 4-chloro-1, 3-dinitrobenzene)

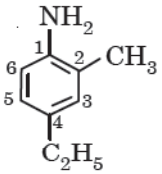

2-Chloro-1-methyl-4--nitrobenzene (**Not:** 4-Methyl -5-chloro-1-nitrobenzene)

- When one of the substituents gives a special name to the molecule (*e.g.* toluene, anisole) then the compound is named as a derivative of that special compound.


2-Chloro-4-nitrotoluene

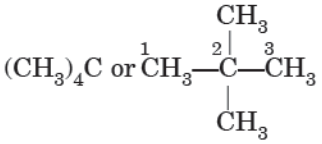

2-Chloro-4-methylanisole


3, 4-Dimethylphenol

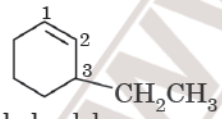

4-Ethyl-2-methylaniline

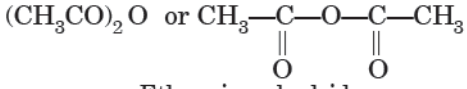
IUPAC NAMES FOR SOME TYPICAL COMPOUNDS

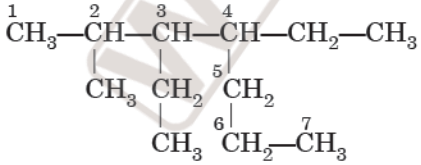
Let us write the IUPAC names of a few typical organic compounds from their structural formulae.

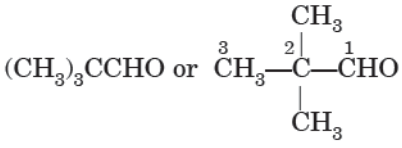

2,2-Dimethylpropane

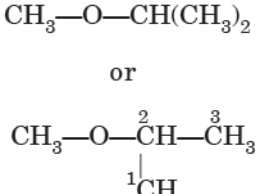
Methylmethanoate

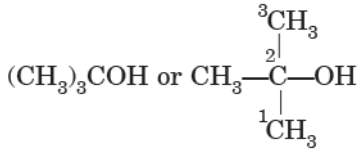

3-Ethylcyclohexene


Ethanoic anhydride


3,4-Diethyl-2-methylheptane


2,2-Dimethylpropanal


2-Methoxypropane


2-Methylpropan-2-ol

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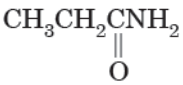
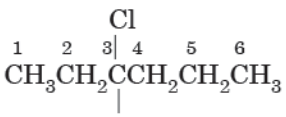
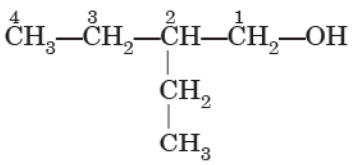
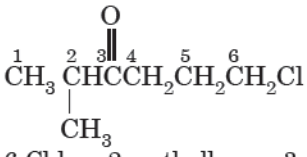

Propanamide


3-Bromo-3-chlorohexane

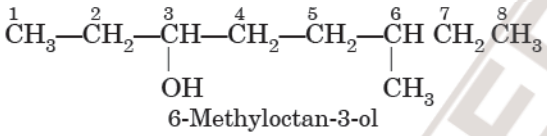
$(C_2H_5)_2CH—CH_2OH$

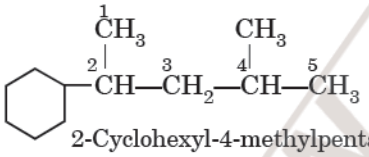
or

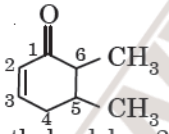

2-Ethylbutan-1-ol

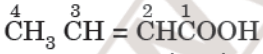

6-Chloro-2-methylhexan-3-one

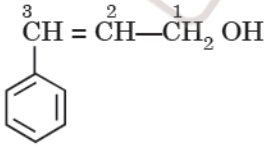
Ethanedial

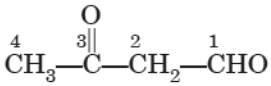

6-Methyloctan-3-ol


2-Cyclohexyl-4-methylpentane

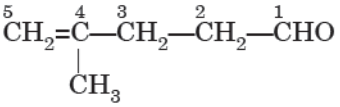

5,6-Dimethylcyclohex-2-en-1-one

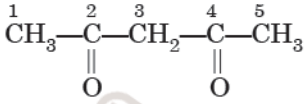

But-2-en-1-oic acid

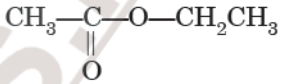

3-Phenylprop-2-en-1-ol

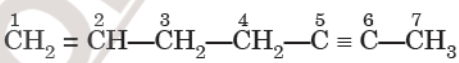

3-Oxobutanal

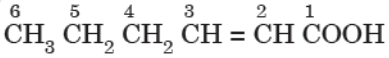
(–CHO is principal group)

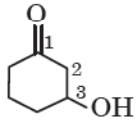

4-Methylpent-4-en-1-al

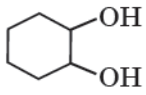

Pentane-2, 4-dione

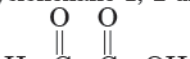

Ethyl ethanoate

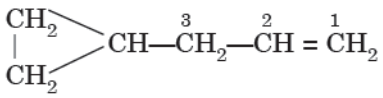

Hept-1-en-5-yne

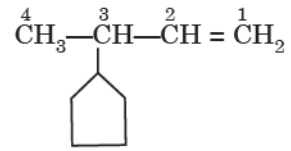

Hex-2-en-1-oic acid

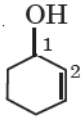

3-Hydroxycyclohexan-1-one


Cyclohexane-1, 2-diol


Formyl methanoic acid


3-Cyclopropylprop-1-ene


3-Cyclopentylbut-1-ene


Cyclohex-2-en-1-ol

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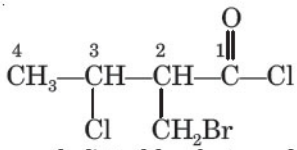
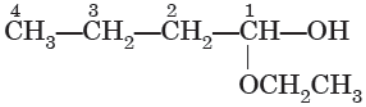
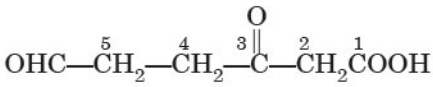
Propanoic anhydride



2-(Bromomethyl)-3-chlorobutanoyl chloride



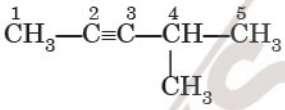
1-Ethoxybutan-1-ol



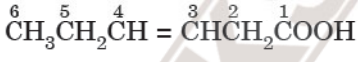
5-Formyl-3-oxopentanoic acid

Some examples of writing structural formulae from the IUPAC names are given below:

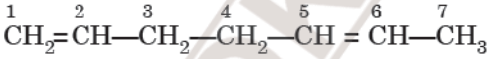
4-Methylpent-2-yne



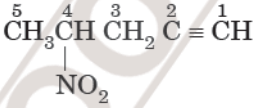
Hex-3-enoic acid



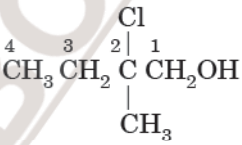
Hepta-1, 5-diene



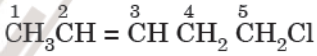
4-Nitropent-1-yne



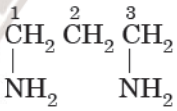
2-Chloro-2-methylbutan-1-ol



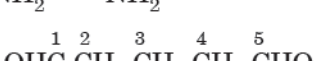
5-Chloropent-2-ene



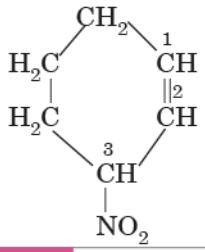
1,3-Diaminopropane



Pentanedial



3-Nitrocyclohexene



SOLVED EXAMPLES

Example 15. *Write the structures for the following :*

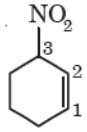
(i) 2-Chlorohexane *(ii) Pent-4-en-2-ol*

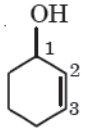
(iii) 3-Nitrocyclohexene *(iv) Cyclohex-2-en-1-ol* *(v) 6-Hydroxyheptanal* ***N.C.E.R.T.***

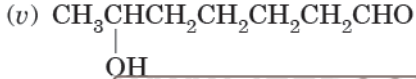
Solution :

(i)

(ii)

(iii) 

(iv) 

(v) 

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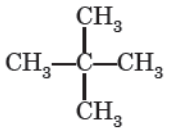
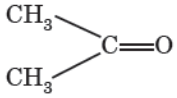
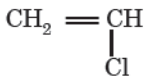
❑ Example 16.

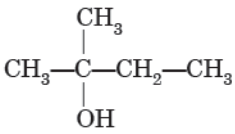
The following organic compounds are popularly known by their common names : (i) Neopentane (ii) Acetone (iii) Vinyl chloride (iv) tert-amyl alcohol (v) iso-butyl bromide (vi) acetonitrile (vii) allyl alcohol (viii) formaldehyde (ix) acetone (x) glycerol. Write their structural formulas and IUPAC names.

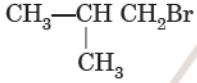
Solution :

(*i*) Neopentane  2, 2-Dimethylpropane

(*ii*) Acetone  Propanone

(*iii*) Vinyl chloride  Chloroethene

(*iv*) *Tert*-amyl alcohol  2-Methylbutan-2-ol

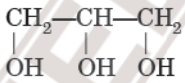
(*v*) Isobutyl bromide  1-Bromo-2-methylpropane

(*vi*) Acetonitrile CH_3CN Ethanenitrile

(*vii*) Allyl alcohol $CH_2{=}CH{-}CH_2OH$ Prop-2-en-1-ol

(*viii*) Formaldehyde HCHO Methanal

(*ix*) Acetylene $HC \equiv CH$ Ethyne

(*x*) Glycerol  Propane-1, 2, 3-triol

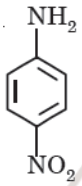
❑ Example 17.

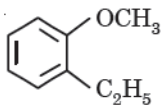
Write the structural formulae of

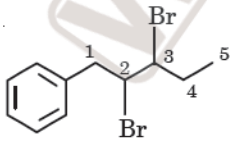
(*a*) *p-Nitroaniline* (*b*) *o-Ethylanisole*

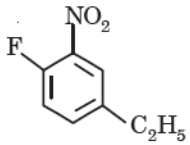
(*c*) *2, 3-Dibromo-1-phenylpentane* (*d*) *4-Ethyl-1-fluoro-2-nitrobenzene* **N.C.E.R.T.**

Solution :

(*a*) 

(*b*) 

(*c*) 

(*d*) 

❑ Example 18.

Give condensed and bond line structural formulae and identify the functional group(s) present if any; for

(*i*) *2, 2, 4-trimethyl pentane* (*ii*) *2-hydroxy-1, 2, 3-propanetricarboxylic acid*

(*iii*) *Cycloocta-1, 5-diene* (*iv*) *Hexanedial*

(*v*) *2-(4-isobutyl phenyl) propanoic acid* **N.C.E.R.T.**

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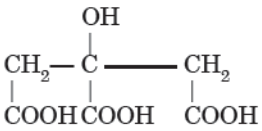
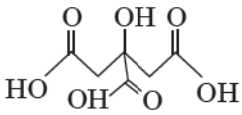
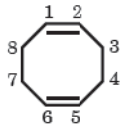
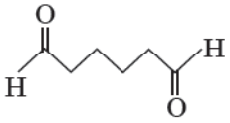
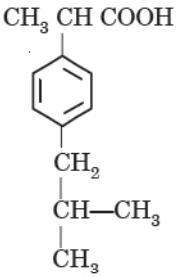
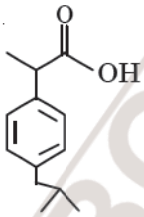
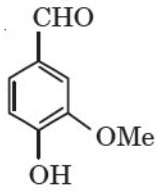
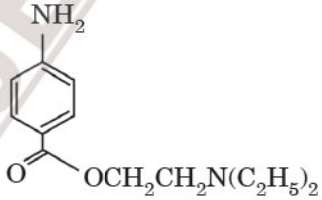
Solution :

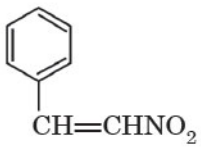
	Condensed structural	Bond line structure	Functional group
(*i*)	$(CH_3)_3C—CH_2\,CH\,(CH_3)_2$		—
(*ii*)			—COOH (carboxyl), —OH (hydroxyl)
(*iii*)	C_8H_{12}		Double bond (=)
(*iv*)	$OCH—(CH_2)_4—CHO$		—CHO (aldehyde)
(*v*)			—COOH (carboxyl)

❑ **Example 19.**

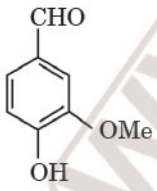
Identify the functional groups in the following compounds :

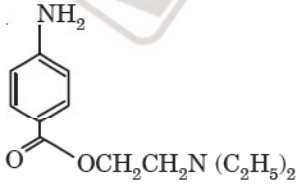
(*a*) 

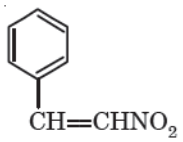
(*b*) 

(*c*) 

Solution :

(*a*)  : —CHO (aldehyde), —OH (hydroxy or alcohol) and –OMe (alkoxy or ether)

(*b*)  : —NH_2 (amino) and —C(=O)—OCH_2CH_2 N $(C_2H_5)_2$; N, N-dialkylaminoester

(*c*)  : —NO_2 (nitro), C=C (alkene) or unsaturated nitro group.

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ISOMERISM

Two or more compounds having the same molecular formula but different physical and chemical properties **are called isomers.**

The phenomenon **of existence of two or more compounds possessing the same molecular formula but different properties** is called **isomerism.**

Types of Isomerism

The isomerism is of two main types :

(a) Structural isomerism

(b) Stereo isomerism

(*a*) **Structural isomerism.** *The compounds having same molecular formula but different structures i.e., different arrangement of atoms or groups of atoms within the molecules are called* ***structural isomers*** *and the phenomenon is called* ***structural isomerism.***

(*b*) **Stereo isomerism.** *The isomers which have the same structural formula but have different relative arrangement of atoms or groups of atoms in space are called* ***stereo isomers*** *and the phenomenon is called* ***stereo isomerism.***

The stereo isomerism is of three types :

(*i*) *Geometrical isomerism,*

(*ii*) *Optical isomerism* and

(*iii*) *Conformational isomerism.*

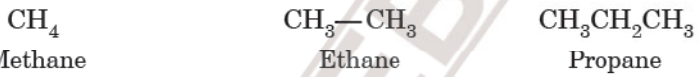
Structural isomerism is discussed in the present unit.

A : Structural Isomerism

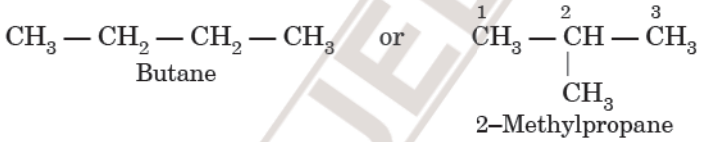
This can be further sub-divided as :

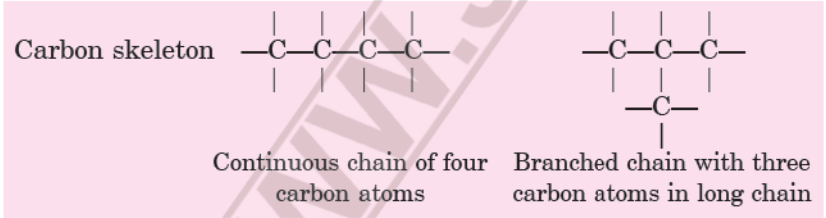
1. Skeletal or chain isomerism. *The compounds having same molecular formula but different arrangement of carbon chain (skeleton) within the molecule are called* ***chain isomers*** *or* ***skeletal isomers*** and the phenomenon is termed as **chain isomerism.**

For example, the first three members of the alkane family (CH_4, C_2H_6 and C_3H_8) do not exhibit chain isomerism because they have only one structural formula.

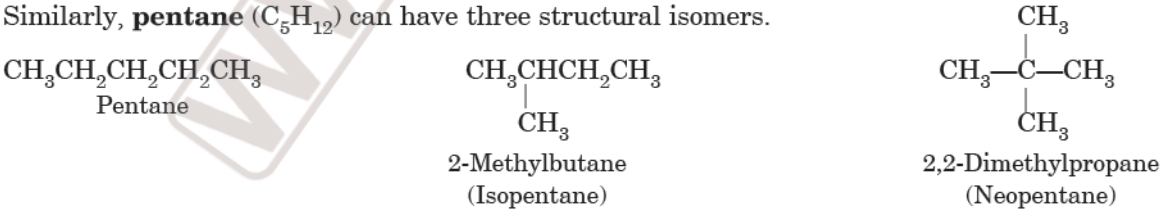


The next member **butane** (C_4H_{10}) can have two structural isomers.



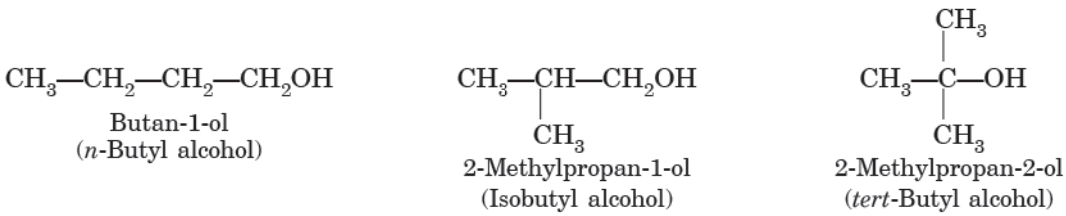


Similarly, **pentane** (C_5H_{12}) can have three structural isomers.



Some other examples are :

(*a*) *C_4H_9OH has three chain isomers.*



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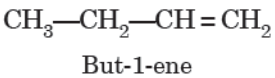
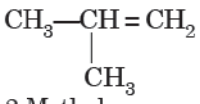
(*b*) *C_4H_8 has two chain isomers.*

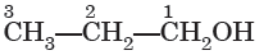


But-1-ene
(Butylene)



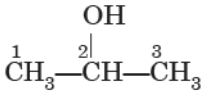
2-Methylpropene
(Isobutylene)

2. Position isomerism. *The compounds which have the same molecular formula but differ in the position of the functional group, carbon-carbon multiple bond or substituent group are called* **position isomers** and this phenomenon is termed as **position isomerism.** For example, the formula, C_3H_7OH represents two position isomers whose structural formulae are given below :

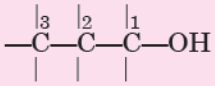


Propan-1-ol
(*n*-Propyl alcohol)

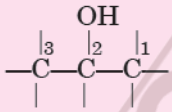
and



Propan-2-ol
(Isopropyl alcohol)



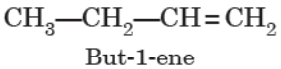
Functional group is at carbon atom 1



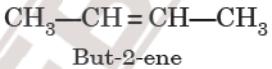
Functional group is at carbon atom 2

Some other examples of position isomers are :

(*a*) *The compound C_4H_8 has two position isomers.*

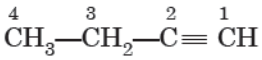


But-1-ene
(α-Butylene)

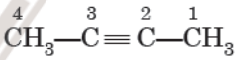


But-2-ene
(Dimethyl ethylene or β-Butylene)

(*b*) *The compound C_4H_6 has two position isomers.*

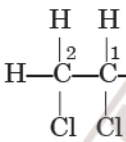


But-1-yne
(α-Crotonylene)

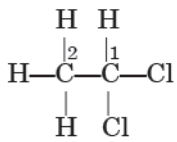


But-2-yne
(Dimethyl acetylene or β-Crotonylene)

(*c*) *The compound $C_2H_4Cl_2$ has two position isomers.*

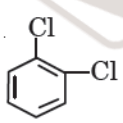


1, 2-Dichloroethane
(Ethylene dichloride)

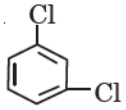


1, 1-Dichloroethane
(Ethylidine dichloride)

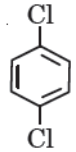
(*d*) In aromatic compounds, the position isomers are observed due to the difference in the position of the substituent groups attached to the benzene ring. For example, $C_6H_4Cl_2$ (dichlorobenzene) has three isomers.



ortho-Dichlorobenzene



meta-Dichlorobenzene



para-Dichlorobenzene

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3. Functional group isomerism. *The compounds having same molecular formula but different functional groups in the molecule* are called **functional group isomers** and this phenomenon is termed as **functional group isomerism.**

For example,

(a) Alcohols and ethers. C_2H_6O represents two isomers having different functional groups.

$CH_3—CH_2OH$ and $CH_3—O—CH_3$

Ethanol (Ethyl alcohol) (*Functional group* —OH)

Methoxymethane (Dimethyl ether) (*Functional group* —O—)

(b) Aldehydes and ketones. C_3H_6O represents two isomers having the structural formulae :

$CH_3—CH_2—\underset{\underset{H}{|}}{C}=O$ and $CH_3—\underset{\underset{O}{\|}}{C}—CH_3$

Propanal (Propionaldehyde) (*Functional group* —CHO)

Propanone (Acetone) (*Functional group* $-\overset{\overset{O}{\|}}{C}-$)

It may be noted that unsaturated alcohols and ethers are also functional isomers of aldehydes and ketones.

$CH_2=CH—CH_2OH$ Prop-2-en-1-ol (Allyl alcohol)

$CH_2=CH—O—CH_3$ Methoxy ethene (Methyl vinyl ether)

(c) Carboxylic acids and esters. The formula $C_2H_4O_2$ represents two isomers having the structural formulae:

$CH_3—\overset{\overset{O}{\|}}{C}—OH$ (Ethanoic acid) (*Acetic acid*) and $H—\overset{\overset{O}{\|}}{C}—OCH_3$ Methyl methanoate (*Methyl formate*)

(*Functional group* $-\overset{\overset{O}{\|}}{C}-OH$) (*Functional group* $-\overset{\overset{O}{\|}}{C}-OR$)

(d) Dienes, allenes and alkynes. Molecular formula C_4H_6 represents three functional isomers:

$\overset{1}{C}H_2=\overset{2}{C}H—\overset{3}{C}H=\overset{4}{C}H_2$ But-1, 3-diene (an alkene)

$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H—\overset{4}{C}H_3$ But-1, 2-diene (an allene)

$CH_3CH_2C\equiv CH$ or $CH_3C\equiv C—CH_3$ (But-1-yne, But-2-yne) (alkynes)

(e) Nitroalkanes and alkyl nitrilies. Molecular formula $C_2H_5NO_2$ represents two functional isomers:

$CH_3—CH_2—\overset{+}{N}\begin{matrix}=O\\ O^-\end{matrix}$ Nitroethane or $CH_3CH_2NO_2$ $CH_3CH_2—O—N=O$ or CH_3CH_2ONO Ethyl nitrile

(f) Cyanides and isocyanides. Molecular formula C_2H_3N shows two functional isomers.

$CH_3—C\equiv N$ Ethane nitrile

$CH_3—N\rightarrow C$ Methyl isocyanide

(g) Primary, secondary and tertiary amines show functional isomerism. For example, C_3H_9N represents three isomers:

$CH_3CH_2CH_2NH_2$ Propan-1-amine (1°-Amine)

$CH_3—CH_2—N\begin{matrix}CH_3\\ H\end{matrix}$ N-Methylethanamine (2°-Amine)

$CH_3—\underset{\underset{CH_3}{|}}{N}—CH_3$ N, N–Dimethylmethanamine (3°-Amine)

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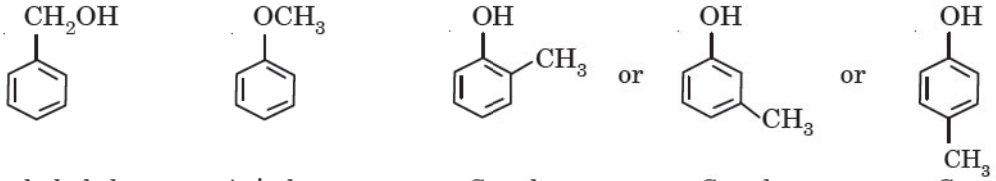
(*h*) Aromatic alcohols and ethers show functional isomerism. For example, molecular formula C_7H_8O represents



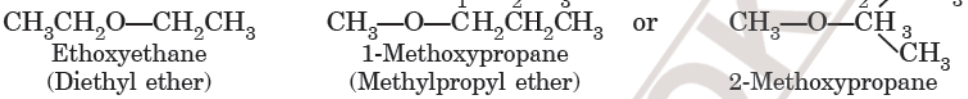
Benzyl alcohol (an alcohol) | Anisole (an ether) | *o*-Cresol (a phenol) | *m*-Cresol (a phenol) | *p*-Cresol (a phenol)

4. Metamerism. *The compounds having same molecular formula but different number of carbon atoms (or alkyl groups) on either side of the functional group,* are called **metamers** and this phenomenon is called **metamerism.** Metamerism is exhibited by the compounds having a bifunctional group *i.e.* —O—, —S—, —NH—, —CO— etc. For example,

(*a*) $C_5H_{10}O$ has two metamers as

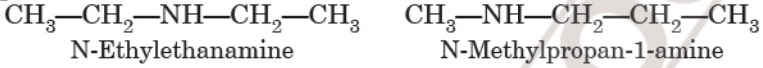
Pentan-3-one | Pentan-2-one (—CO has different alkyl groups around it)

(*b*) $C_4H_{10}O$ has two metamers as



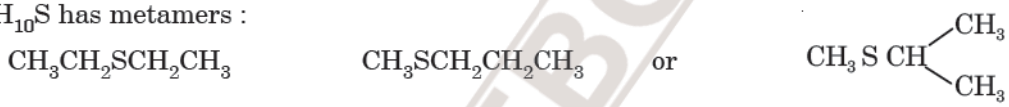
Ethoxyethane (Diethyl ether) | 1-Methoxypropane (Methylpropyl ether) | 2-Methoxypropane (Isopropyl methyl ether)

(*c*) $C_4H_{11}N$ has two metamers as



N-Ethylethanamine | N-Methylpropan-1-amine

(*d*) $C_4H_{10}S$ has metamers :



Diethyl thioether | Methyl *n*-propyl thioether | Isopropyl methyl thioether

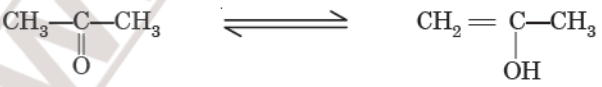
It may be noted that some compounds exhibit both position isomerism as well as metamerism. For example

Pentan-2-one and Pentan-3-one are position isomers as well as metamers

5. Tautomerism. *This is a special type of functional isomerism in which the isomers differ in the arrangement of atoms but they exist in dynamic equilibrium with each other and this phenomenon is termed as* ***tautomerism***. For example, acetaldehyde and vinyl alcohol are tautomers which exist in equilibrium as :

Acetaldehyde | Vinyl alcohol

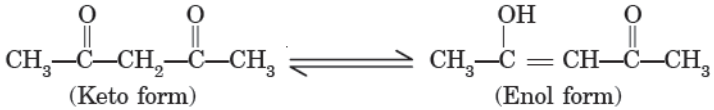
Similarly,



Propanone | Prop-1-en-2-ol

Cyclohexanone | Cyclohex-1-en-1-ol

Acetyl acetone exists in two forms as :



(Keto form) | (Enol form)

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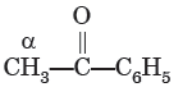
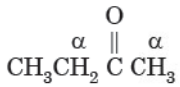
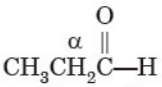
When one of the tautomers exists in *keto* form and the other in the *enolic form*, then tautomerism is also called **keto-enol tautomerism.**

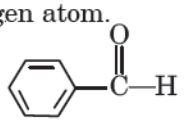
It may be noted that only those carbonyl compounds exhibit keto-enol tautomerism which have at least one acidic α-hydrogen *i.e.* α-hydrogen on a saturated carbon. Thus, acetophenone, butan-2-one, propanal, etc, exhibit keto-enol tautomerism.

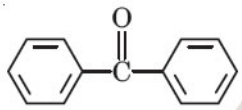

Acetophenone


Butan-2-one


Propanal

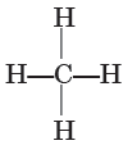
On the other hand, benzophenone, benzaldehyde, etc. do not show keto-enol tautomerism because these do not have α-hydrogen atom.

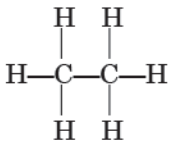

Benzaldehyde

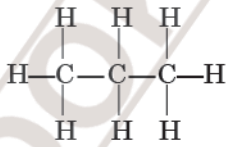

Benzophenone

Structural Isomerism in Alkanes

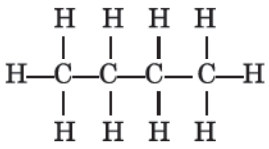
The alkanes show structural isomerism *in which the isomers differ in the skeletons of carbon atoms*. This is also known as **chain isomerism**. For example, the first three members of the family (CH_4, C_2H_6 and C_3H_8) do not exhibit chain isomerism because they have only one structural formula :


Methane

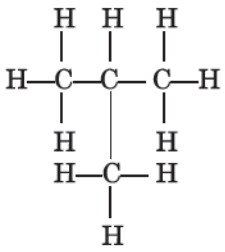

Ethane


Propane

Butane (C_4H_{10}) can have **two** structural isomers :


or $CH_3—CH_2—CH_2—CH_3$

Butane

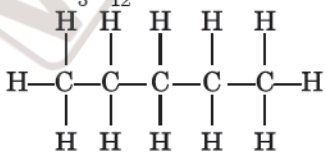

or $CH_3—CH(CH_3)—CH_3$

2-Methylpropane

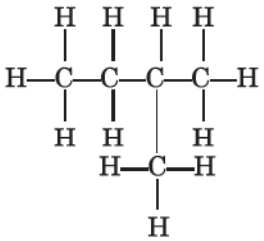
The two isomers differ in the chain of carbon atoms as :

Straight chain — Branched chain

Similarly, **pentane** (C_5H_{12}) has **three isomers**.


or $CH_3—CH_2—CH_2—CH_2—CH_3$

Pentane


or $CH_3—CH_2—CH(CH_3)—CH_3$

2-Methylbutane

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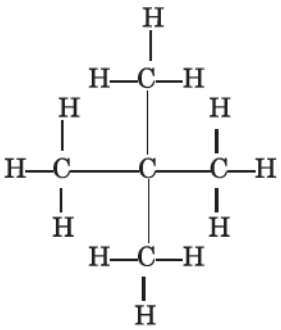
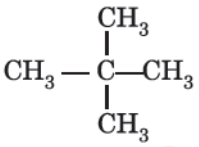
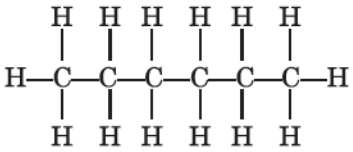


or 

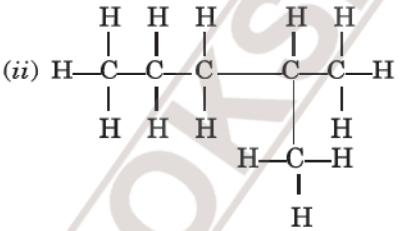
2-2-Dimethylpropane

Hexane (C_6H_{14}) has **five st ructural isomers**

(*i*) 

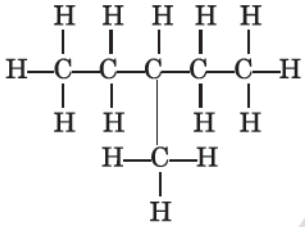
or $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

Hexane

(*ii*) 

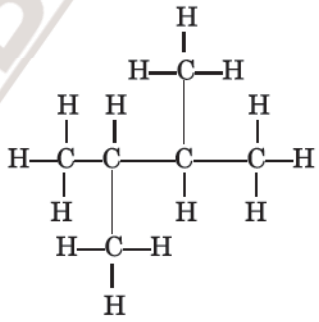
or $CH_3 - CH_2 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH_3$

2-Methylpentane

(*iii*) 

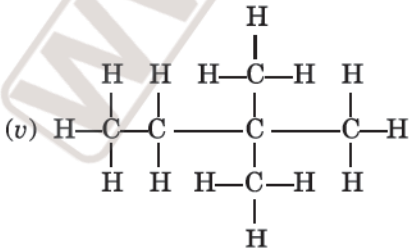
or $CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_2-CH_3$

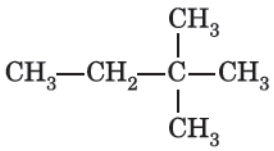
3-Methylpentane

(*iv*) 

or $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH_3$

2,3-Dimethylbutane

(*v*) 

or 

2, 2-Dimethylbutane

It is clear that as the number of carbon atoms increases, the number of chain isomers also increases. For example, C_7H_{16} has **nine**, C_8H_{18} has eighteen chain isomers. The hydrocarbon $C_{10}H_{22}$ has 75 structural isomers.

B : Stereoisomerism

These are the compounds which have the same constitution (structural formula) and sequence of bonds but differ in the relative positions of atoms or groups of atoms in space. The common example of stereoisomerism

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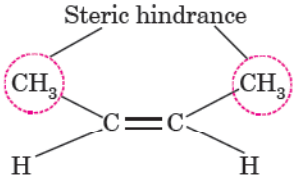
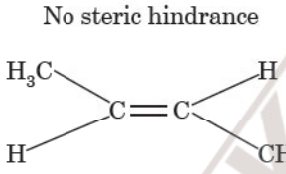
is geometrical isomerism exhibited by alkenes. As will be studied (Unit-13) the compounds containing double bond (alkenes) show *cis-trans isomerism*. This is due to the restricted rotation around carbon-carbon double bond. As a result, the positions of the groups attached to these carbon atoms are fixed in space. This type of isomerism is also called **geometrical isomerism.** Stereoisomerism will be discussed in detail in next class.

One of the consequences of geometrical isomerism is **steric hindrance.** This is due to the fixed positions of atoms or groups of atoms around carbon-carbon double bond. It is known that two atoms or groups of atoms in an organic molecule at a distance less than or equal to the sum of the van der Waals radii repel each other due to spatial crowding. This repulsion is known as **steric hindrance** or **steric strain** or **van der Waals strain**. Larger is the size of the group, greater will be the steric hindrance. Molecules having steric hindrance are relatively less stable than those which do not have steric hindrance. For example, *cis*-But-2-ene has steric hindrance while *trans*-But-2-ene does not have any steric hindrance.

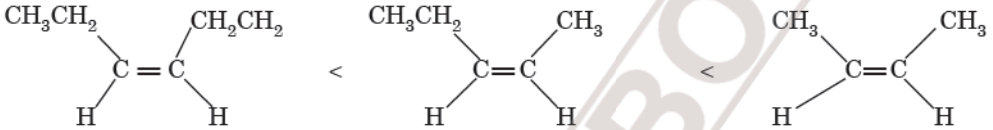


cis-But-2-ene
(less stable)



trans-But-2-ene
(more stable)

Similarly, *cis*-Pent-2-ene is less stable than but-2-ene and hex-3-ene is even less stable than pent-2-ene. This is due to larger steric hindrance of bulky groups.



Hex-3-ene Pent-2-ene But-2-ene

Steric effects greatly influence the structure and reactivity of organic compounds.

To Sum Up

Isomerism

STRUCTURAL ISOMERISM

- Chain isomerism
- Position isomerism
- Functional isomerism
- Metamerism
- Tautomerism

STEREOISOMERISM

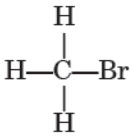
- Geometrical isomerism
- Optical isomerism

SOLVED EXAMPLES

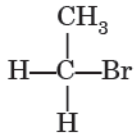
Example 20.

Draw the structures of bromomethane, bromoethane, 2-bromopropane and tert-butyl bromide. Arrange these in order of increasing steric hindrance.

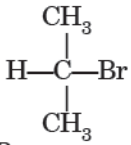
Solution :



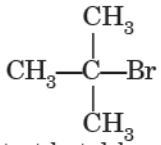
Bromomethane
(No steric hindrance)



Bromoethane
(Small steric hindrance)



2-Bromopropane
(More steric hindrance)



tert-butyl bromide
(Most steric hindrance)

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Thus, the steric hindrance increases as :
bromomethane < bromoethane < 2-bromopropane < tert-butyl bromide.

ELECTRON DISPLACEMENTS IN COVALENT BONDS

Organic compounds mainly consist of covalent bonds. The electron pairs in these covalent bonds may undergo displacements either of their own or under the influence of other species (atom or group of atoms) or in the presence of an appropriate attacking reagent. Four types of electron displacements are generally noticed in the mechanism of organic reactions. These are given below :

1. Inductive Effect

This is a **permanent effect** which arises whenever an electron withdrawing group (electronegative atom such as halogen) is attached to the end of a carbon chain. To understand this, let us consider a chain of carbon atoms having Cl atom at one end :

C—C—C—C—Cl

We know that chlorine is more electronegative than C. Due to larger electronegativity of Cl, the electron pair shared between C_1 and Cl will be displaced towards Cl atom. As a result of this, Cl acquires a partial negative charge (δ–) and C acquires a partial positive charge (δ+). This displacement is however, not limited to C_1—Cl bond but is transmitted to other carbon atoms along the chain. This is because, the small positive charge on C_1 will attract the σ-electrons of the C_1—C_2 bond towards it. As a result of this displacement, the positive charge on C_1 is partially neutralised while a small positive charge is developed on C_2. The charge on C_2 is less than that on C_1 (δ'+ < δ+). Similarly, C_3 will acquire a small positive charge δ+" (δ+" < δ'+). Such a polarisation of σ-bond caused by the polarisation of adjacent σ-bond is called inductive effect. Thus,

the process of displacement of σ–electrons along the saturated carbon chain due to the presence of a polar covalent bond at one end of the chain is called **inductive effect** and is denoted as **I effect**.

This is a permanent effect and is generally represented by an arrow with its head in the middle of the covalent bond pointing in the direction of electron displacement as shown below :

$$\overset{\delta+'''}{\text{—C}}\rightarrow\overset{\delta+''}{\text{C}}\rightarrow\overset{\delta+'}{\text{C}}\rightarrow\overset{\delta+}{\text{C}}\rightarrow\overset{\delta-}{\text{Cl}} \qquad (\delta+''' < \delta+'' < \delta+' < \delta+)$$

However, it may be noted that **this effect decreases sharply as we move away from the atoms involved in the initial polar bond and becomes negligible from the fourth atom onwards.**

Types of Inductive Effects

The inductive effect is related to the ability of the substituent to either *withdraw* or *donate* electron density to the attached carbon atom. Based on this ability, the substituents may be classified as **electron withdrawing** or **electron donating groups** relative to hydrogen. For comparing the relative effects, hydrogen is taken as standard.

The substituents having electron attracting power more than hydrogen are called electron withdrawing substituents. For example, groups such as halogens, nitro (–NO_2), cyano (–CN), carboxy (–COOH), ester (–COOR), aryloxy (–OAr, e.g., –OC_6H_5) are electron withdrawing groups.

On the other hand, *the* ***substituents having electron attracting power less than hydrogen*** *are called* **electron donating groups**. For example, alkyl groups such as methyl (–CH_3), ethyl (–C_2H_5), isopropyl [–$CH(CH_3)_2$], *t*-butyl [–$C(CH_3)_3$] etc. are electron donating groups.

Based on the type of substituents, there are two types of inductive effects designated as **–I effect** and **+ I effect**.

(i) If the substituent attached to the end of the carbon chain **is electron withdrawing**, the effect is called **–I (or electron withdrawing) effect**. For example,

$$\text{C}\rightarrow\text{C}\rightarrow\text{C}\rightarrow\overset{\delta-}{\text{X}}$$ (electron withdrawing substituent) **–I effect**

The –I effect of some substituents in the decreasing order w.r.t. hydrogen is:

—NO_2 > —CN > —COOH > —COOR > —F > —Cl > —Br > —I > —OH > —OCH_3 > —C_6H_5 > H

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(ii) If the substituent attached to the end of the carbon chain **is electron donating** group, the effect is called **+ I (or electron donating) effect.** For example,

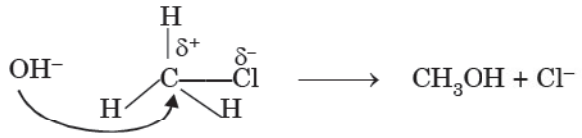
$$C \leftarrow C \leftarrow C \overset{\delta^-}{\leftarrow} CH_3 \text{ (electron donating substituent)}$$ +I effect

The +I effect of some substituents in the decreasing order w.r.t. hydrogen is

$$(CH_3)_3C— > (CH_3)_2CH— > CH_3CH_2— > CH_3—$$

It is clear that the more substituted the alkyl group, stronger is its + I effect.

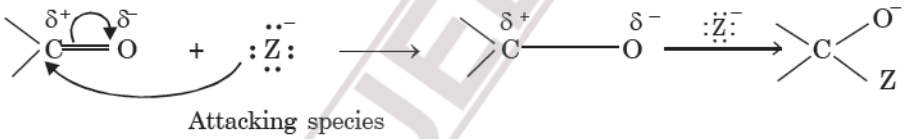
The inductive effect plays very significant role in organic chemistry in understanding reactions. Carbon of methyl chloride, for example, acquires partially positive charge due to shift of electrons towards chlorine and provides a site for attack by a negatively charged species (say OH^-).



2. Electromeric Effect

It is a **temporary effect** which takes place between two atoms joined by a multiple bond, *i.e.,* a double or a triple bond. This *occurs at* the requirements of the attacking reagent and involves instantaneous transfer of a shared pair of electrons of the multiple bond to one of the linked atoms. However, when the attacking reagent is removed, the molecule acquires its original electronic condition.

As an example, consider the carbonyl group, >C=O, present in aldehydes and ketones. When a negatively charged reagent seeking positive site, say :X: approaches the molecule, it causes instantaneous shift of electron pair of carbonyl group to oxygen (more electronegative than carbon). As a result, the carbon becomes deprived of its share in this transferred pair of electrons and



thus acquires positive charge while oxygen which has taken complete control of the electron pair becomes negatively charged. Therefore, in the presence of attacking reagent, one bond is lost. Then the negatively charged attacking reagent links to the carbon having positive charge.

The phenomenon of movement of electrons from one atom to another in a multiple bond at the demand of attacking reagent is called **electromeric effect** and is denoted as **E effect.**

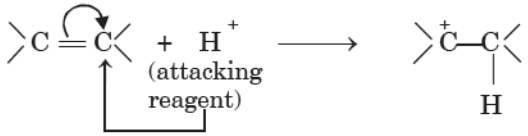
The electromeric shift of electrons occurs only at the moment of the reaction.

Like the inductive effect, the electromeric effect is also classified as :

(i) Positive electromeric effect or + E effect

(ii) Negative electromeric effect or – E effect

(i) Positive electromeric effect (+E effect). *When the electrons of the π-bond are transferred to the atom to which the attacking reagent finally gets attached, the effect* is called +E(positive electromeric). For example, the addition of H^+(acids) to alkenes.



+E effect

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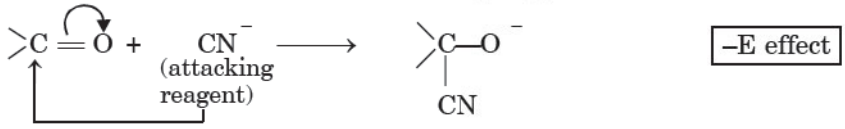
(*ii*) ***Negative electromeric effect (–E effect).*** *When the electrons of the π-bond are transferred to the atom other than the one to which the reagent gets finally attached,* the effect is called **–E (negative electromeric)** effect. For example, the addition of CN^- to the carbonyl group,



–E effect

Thus, it may be concluded that electromeric effect is said to be **+E-effect** when displacement of electrons is towards the atom or group and **–E-effect** when it is away from the atom or group on which attacking reagent is added.

Differences between Inductive effect and Electromeric effect

Inductive effect	Electromeric effect
1. It is a permanent effect which involves slight drifting of shared σ-electrons towards more electronegative atom.	1. It is a temporary effect which involves complete transfer of π-electrons to one of the bonded atoms.
2. It operates only in saturated compounds which contain at least one polar bond.	2. It operates in unsaturated compounds which contain at least one multiple bond which may be polar or non-polar.
3. It does not need any outside reagent for its operation.	3. It operates only in the presence of an outside reagent.
4. It involves a partial separation of charges without formation of ions.	4. It involves complete transfer of electrons from the reagent to substrate and vice versa. As a result of this effect, ions are formed.

3. Resonance or Mesomeric Effect

There are many molecules whose behaviour cannot be explained by a single Lewis structure. To explain their behaviour two or more than two structures may be proposed (Unit IV) and the actual molecule is said to be resonance hybrid of these structures. This phenomenon is called **resonance.** Thus

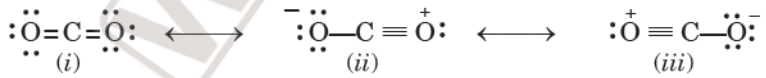
if a molecule can be assigned two or more structures, none of which is capable of describing all the known properties of the compound, then the actual structure is intermediate or resonance hybrid of these structures. This phenomenon is called **resonance.**

The various structures written are called **resonating structures.**

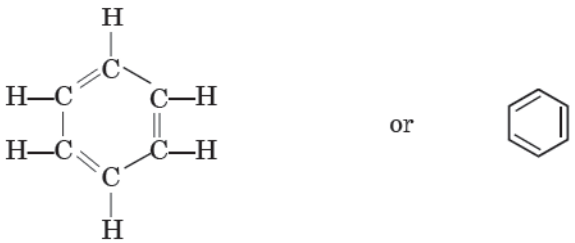
The phenomenon of resonance can be explained with the help of **CO_2 molecule**. It has been represented by the structural formula :

Though this satisfies the conventional valency requirements, yet it cannot explain some experimental facts. The actual carbon-oxygen bond in CO_2 has been found to be 115 pm whereas the normal carbon-oxygen double bond is 122 pm and that for triple bond is 110 pm. This means that carbon oxygen bond in carbon dioxide is intermediate between a double and a triple bond. To account for this, two other structures were proposed :

The actual molecule is said to be a resonance hybrid of these three structures :



Let us consider another example of benzene. It may be represented by a cyclic structure having alternate C—C single and C = C double bonds.



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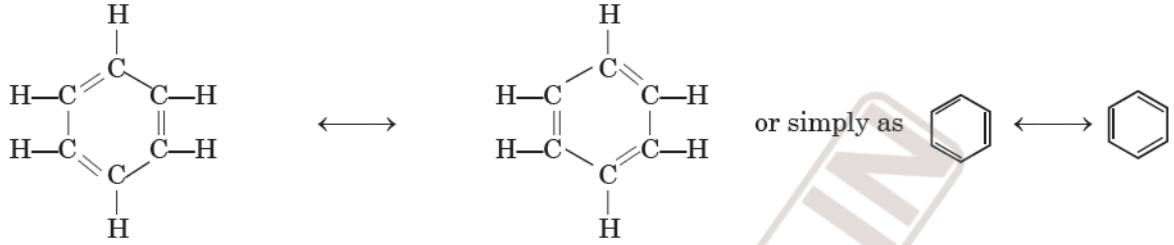
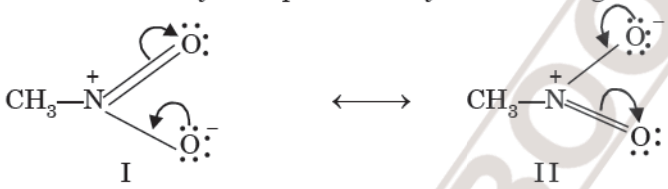
Therefore, we expect two different bond lengths of carbon-carbon bonds due to C—C single and C = C double bonds. However, as determined experimentally, benzene has a uniform C—C bond distance of 139 pm. This value is intermediate between the C—C single (154 pm) and C = C double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by a single structure. The benzene molecule may be regarded as resonance hybrid of the following two structures :



The resonating structures of carboxylic acid may be written as :

Similarly, nitromethane may be represented by the following resonating structures :

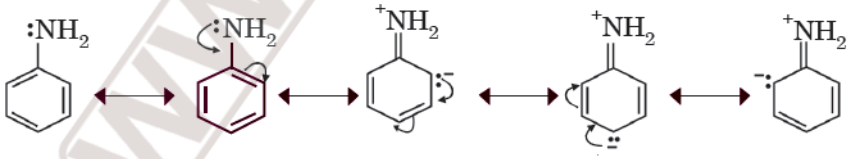


The structures I and II have two types of NO bonds. However, it is known that two N–O bonds of nitromethane are of the same bond length which is intermediate between a N–O single and a N=O double bond. The actual structure of nitromethane is regarded as the resonance hybrid of structures I and II.

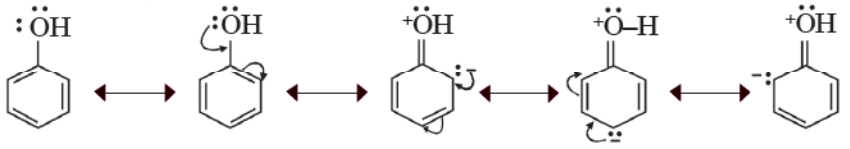
The resonance structures of acetate ion (CH_3COO^-), aniline ($C_6H_5NH_2$) and phenol (C_6H_5OH) are shown below :

Acetate CH_3COO^- ion

Aniline $C_6H_5NH_2$ molecule



Phenol C_6H_5OH molecule



It may be noted that the energy of the actual structure of the molecule *i.e.* resonance hybrid is lower than that of any of the resonating structures. *The difference in energy between the actual structure and the most stable of the resonating structures is* called **resonance energy** or **resonance stabilisation energy**. The different resonance structures contribute to the actual structure in proportion to their stability.

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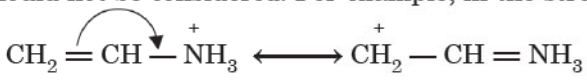
Rules for writing resonance structures

The following rules are applied for writing resonance structures :

1. The resonance structures should have same positions of nuclei.
2. All the resonance structures should have same number of unpaired electrons.
3. The contributing structures should have nearly same energy.
4. All the atoms should have octet of electrons (except hydrogen which has duplet). The resonance structures which violate octet rule should not be considered. For example, in the structures :

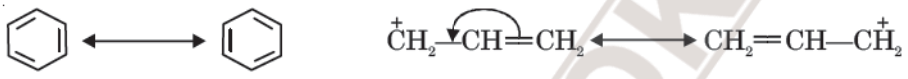


I II

Structure II cannot be considered as a resonance structure because it has 10 electrons around nitrogen and hence violates the octet rule. As we know, nitrogen cannot have more than 8 electrons because it does not have *d*-orbitals.

Relative Contribution of Resonance Structures

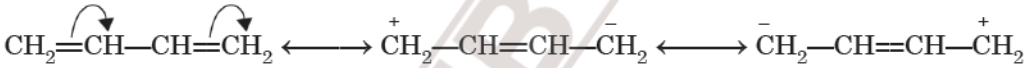
(*i*) *Structures which are indistinguishable are of equal energy and hence contribute equally towards resonance hybrid*. For example, structures I and II for benzene or III and IV for allylic carbocation contribute equally.



I II III IV

Benzene Allylic carbocation

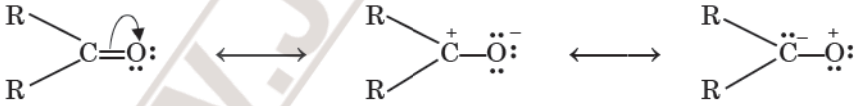
(*ii*) *Structures with more number of covalent bonds contribute more towards the resonance hybrid.* For example, 1,3-butadiene may be represented by the following structures :



I II III

Structure I makes more contribution towards resonance hybrid because it has two π-bonds (11 covalent bonds) than structures II and III which have only one π-bond each (10 covalent bonds).

(*iii*) *The structures with negative charge on the more electronegative atom and the positive charge on less electronegative atom are of lower energy and hence contribute more towards the resonance hybrid.* For example, ketones may be represented as :



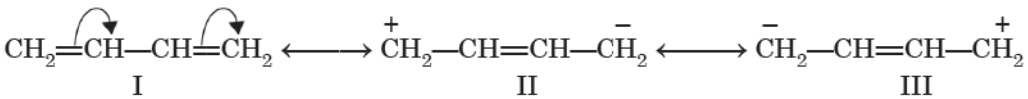
I II III

In these structures, the structure III contributes least because it has positive charge on the more electronegative oxygen atom and a negative charge on less electronegative carbon atom. Similarly, among the structures :

I II

both have same number of covalent bonds and make significant contribution. However, structure II has more contribution because negative charge is on more electronegative O atom.

(*iv*) *Structures which involve separation of positive and negative charges are of higher energy and contribute less towards resonance hybrid.* For example, in case of 1, 3-butadiene, structures II and III contribute less than structure I because these involve separation of charges.



I II III

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Similarly for carboxylic acids, structure II involves separation of charges and hence contributes much less than structure I.

I Carboxylic acid (more stable) ⟷ II (less stable)

(*v*) *Structures having like charges on adjacent atoms are highly unstable and hence contribute* less towards resonance hybrid. For example, structure II makes negligible contribution towards the resonance hybrid of diketone.

I 1, 2-Diketone ⟷ II (negligible contribution)

(*vi*) *Structures in which the positive charge is delocalised over two or more atoms make important contribution towards resonance hybrid.* For example, the structure (II) makes significant contribution towards the resonance hybrid of the carbocation (I) because it helps to disperse the positive charge.

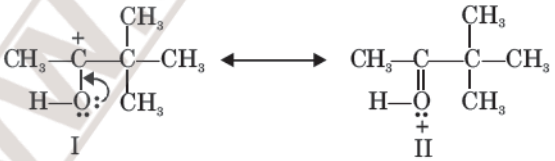
I ⟷ II

It may be noted that though structure II has positive charge on electronegative atom, yet its contribution is significant towards the resonance hybrid because it helps in dispersal of charge.

(*vii*) *Resonance structures in which each atom has complete octet of electrons are more stable and contribute more to resonance hybrid.* For example,

(Less stable) (More stable)

In structure II, the octet of all atoms is complete and therefore, it contributes more towards resonance hybrid. Similarly, in the following carbocation, structure II makes significant contribution because in it every atom (except hydrogen) has a complete octet of electrons.



I (Less stable) ⟷ II (More stable)

Resonance Effect or Mesomeric Effect

Resonance effect is the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and a lone pair of electrons present on an adjacent atom. This effect is transmitted through the chain. This is very significant in case of conjugated systems (having alternate σ and π-bonds). The electrons can flow from one part of the system to the other due to resonance.

There are two types of resonance or mesomeric effect designated as R or M effect :

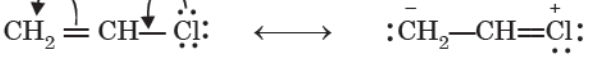
(*i*) Positive resonance effect (+ R effect)

(*ii*) Negative resonance effect (–R effect)

(*i*) Positive resonance effect (+ R effect)

If a substituent has tendency to donate electrons to the double bond or conjugated system, the effect is called **positive resonance effect** or **+ R effect.** For example, groups such as

—OH, —OR, —NH_2, —NHR, —NR_2, —Cl, —Br, —I, etc, show + R effect.

e.g.,  +R effect

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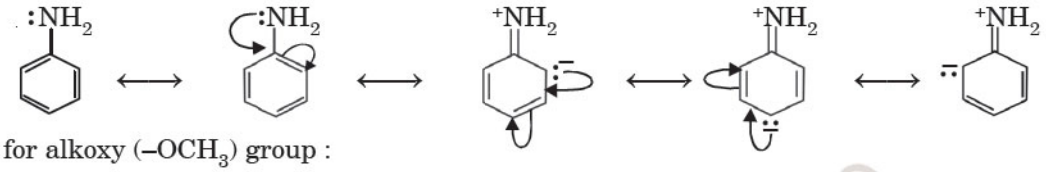
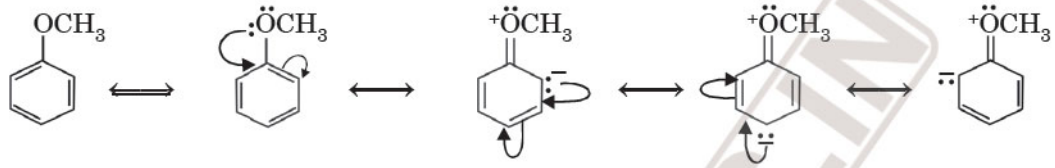
In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. In case of benzene ring, this results into certain positions of high electron densities in the ring. For example, this effect is shown for aniline :



Similarly, for alkoxy ($-OCH_3$) group :



Donation of electrons into a benzene ring by resonance

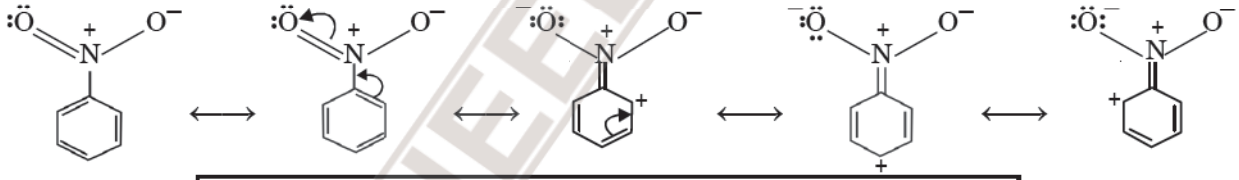
***(ii)* Negative resonance effect (–R effect)**

If a substituent has tendency to withdraw electrons from a double bond or a conjugated system towards itself, the effect is called **negative resonance effect** or **–R effect**. For example, groups such as

$-\overset{|}{C}=O$, —CHO, —CN, $-NO_2$, —COOR, etc, show –R effect.

e.g., –R effect

In this effect, the transfer of electrons is towards the atom or substituent group attached to the conjugated system. In case of benzene ring, this effect results into certain positions of low electron densities in the ring. For example, this effect is shown by -nitro group in benzene as :



Withdrawal of electrons from a benzene ring by resonance

Differences between Inductive effect and Resonance effect

	Inductive effect	Resonance effect
1.	This effect involves displacement of σ-electrons.	The resonance involves displacement of π-electrons or lone pair of electrons.
2.	It operates in saturated compounds.	It operates only in unsaturated conjugated systems.
3.	This effect moves upto three carbon atoms and becomes negligible from the fourth carbon atom onwards.	This effect moves all along the length of the conjugated system.
4.	This effect causes slight drift of σ-electrons towards the more electronegative atom and hence only partial charges (δ+ and δ–) are developed.	This results in complete transfer of electrons and hence full +ve and –ve charges are developed.

The effect of these will be discussed later on.

4. Hyperconjugation

When a H – C bond is attached to an unsaturated system such as double bond or a benzene ring, the sigma (σ) electrons of the H – C bond interact or enter into partial conjugation with the unsaturated system. ***The interactions between the electrons of π systems (multiple bonds) and the adjacent σ bonds (single H–C bonds) of the substituent groups in organic compounds*** is called **hyperconjugation.**

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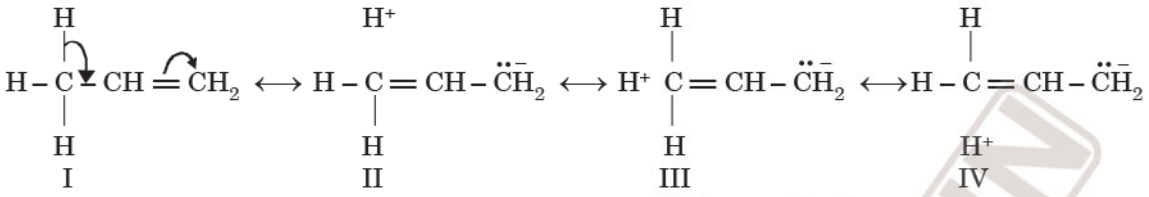
The concept of hyperconjugation was developed by Baker and Nathan and is also known as **Baker and Nathan effect.**

According to this concept, if an alkyl group carrying at least one hydrogen atom is attached to an unsaturated carbon atom, it releases electrons of carbon - hydrogen single bond towards the multiple bond. For example, the hyperconjugation in propene is shown below :



The various hyperconjugation forms of propene are called **contributing structures** or **hyperconjugative structures.** In fact hyperconjugation effect is similar to resonance effect. Since there is no bond between the α-carbon atom and one of the hydrogen atoms, the hyperconjugation is also called **no-bond resonance.** However, *it may be noted that although a free proton has been shown in the above structures, it is still bound quite firmly to the π-cloud and hence is not free to move.*

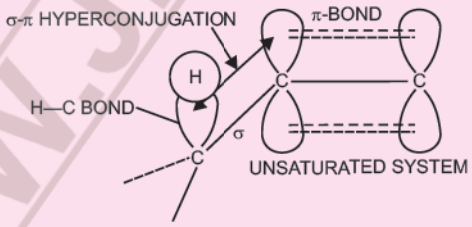
It is clear from the above structures that hyperconjugation occurs through the H-atoms present on the carbon atom next to the double bond is **α-hydrogen atoms.** Therefore, more the number of α-hydrogen atoms, more are the number of hyperconjugative structures. Thus, hyper conjugation effect is expected to be more due to CH_3- (methyl) group than due to CH_3CH_2- (ethyl) group because the latter has only two H atoms attached to the α - carbon atom. In a similar manner, the hyperconjugation effect will be less if $(CH_3)_2CH-$ (*iso*-propyl) group is attached to unsaturated system and there will be no hyperconjugation effect if $(CH_3)_3C-$ (*tert*-butyl) group is attached to the α-carbon of unsaturated system.

Thus, the order of hyperconjugation effect decreases in the order is :

$$CH_3- > CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$$

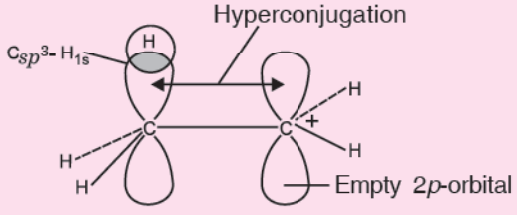
Orbital concept of hyperconjugation

The orbital concept of hyperconjugation may be explained with the help of propene. In this, the electron pair of C – H bond (σ - bond) is involved in conjugation with the π-electron pair of the double bond. Therefore, hyperconjugation involves delocalisation of σ-electrons of H – C bond through overlapping of *p*-orbitals of double bond as shown below:



Orbital representation of σ- π hyperconjugation

Hyperconjugation is also possible in organic compounds in positively charged carbon atom which has an empty *p*-orbital. To understand this, let us consider $CH_3CH_2^+$ (ethyl carboation). One of the C—H bonds of the methyl group can align in plane of the empty *p*-orbital and the electrons constituting the C—H bond in plane with this *p*-orbital can then be delocalised into the empty *p*-orbital. Therefore, in this case, hyperconjugation arises due to the partial overlap of a sp^3-*s* (a C—H bond) with the empty *p*-orbital of an adjacent positively charged carbon atom.



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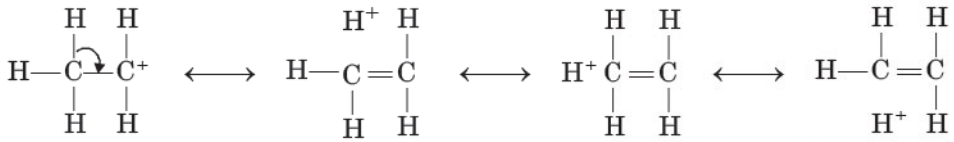
The hyperconjugation in ethyl carbocation may be represented as :



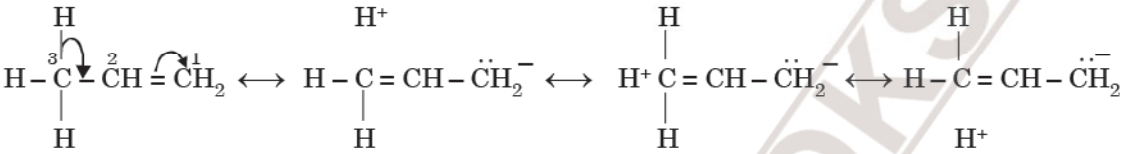
This type of overlap stabilises the cation because the electron density from the adjacent σ bond helps in dispersing the positive charge. Thus, in general, larger the number of alkyl groups attached to the positively charged carbon atom, greater is the hyperconjugation interaction and consequently greater the stabilisation of the cation. Thus, the stability of the carbocation decreases as :

$$(CH_3)_3C^+ > (CH_3)_2\,CH^+ > CH_3CH_2^+ > CH_3^+$$

Applications of Hyperconjugation

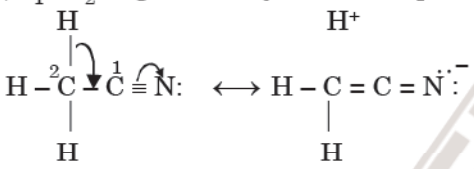
The concept of hyperconjugation is very useful in explaining stabilities of some organic molecules.

(*i*) **Shortening of carbon-carbon single bonds adjacent to multiple bonds.** In propene, the carbon-carbon bond adjacent to double bond acquires some double bond character and hence is little shorter.

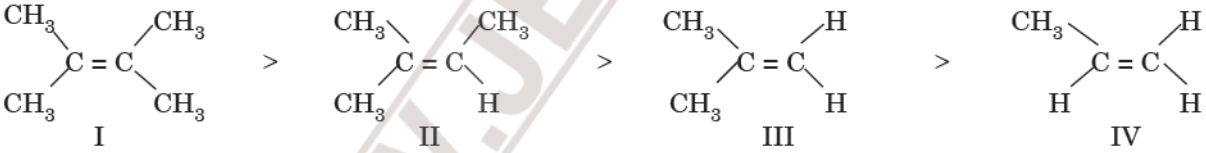


Due to hyperconjugation, the bond length of the carbon-carbon bond between C-2 and C-3 in propene is 149 pm, which is less than the normal carbon-carbon bond length (154 pm) in propane.

Similarly, $C_1 - C_2$ single bond adjacent to a triple bond, for example in acetonitrile, is shorter than normal bond.



(*ii*) **Relative stability of methylated alkenes.** Larger the number of methyl groups linked to carbon-carbon double bond, more is the number of hyperconjugative C – H bonds and greater is the stability of alkene. Thus, the stability of alkenes is :



I — 2, 3 - Dimethylbut - 2 - ene

II — 2 - Methylbut - 2 - ene

III — 2 - Methylpropene

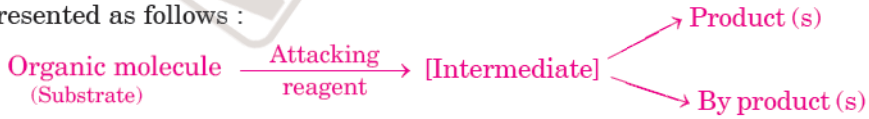
IV — Propene

This order of stability is because of greater number of contributing structures, causing larger delocalisation and hence stability of alkene. For example, alkene - I has 12 α - hydrogens while alkene-II has nine α - hydrogen atoms. Therefore, there will be larger hyperconjugation in alkene - I and will be more stable than alkene-II.

Hyperconjugation can also explain relative stabilities of carbocations and free radicals as discussed later.

FUNDAMENTAL CONCEPTS IN ORGANIC REACION MECHANISM

In an organic reaction, the organic molecule (known as **substrate**) reacts with an attacking reagent and leads to the formation of one or more **intermediates** and finally the **products**. The general raction may be represented as follows :



The **substrate is that reactant which provides carbon to the new bond and the other reactant is** called **reagent**. However, if both the reactants supply carbon to the new bond then choice of substrate is arbitrary and in that case, the molecule which we are interested to study is the substrate.

During organic reactions, a covalent bond between two carbon atoms or a carbon atom and some other atom is broken and a new bond is formed.

The detailed study of stepwise description of a reaction, electron movement, energetics during bond breaking and bond formation and the details of time required for the steps, when a reactant is transformed into the product is called reaction mechanism.

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The knowledge of reaction mechanism is very important because it helps to understand the reactivity of organic compounds.

TYPES OF BOND FISSION

Organic reactions usually involve making and breaking of covalent bonds. The fission of bonds can take place in two ways :

1. Homolytic fission 2. Heterolytic fission

1. Homolytic fission

In homolytic fission, *the cleavage of covalent bond between two atoms takes place in such a way that each bonded atom retains one electron of the shared pair.* This is a symmetrical fission and leads to the formation of neutral species (atoms or groups of atoms) having unpaired electrons. These species are called **free radicals.** The free radicals are denoted by putting dot over the symbol of atom or group of atoms. The single electron movement is shown by "half headed" curved arrows (⟶). For example,

Half headed arrows (⟶) indicate single electron movement.

$$A \cdot\!|\!\cdot B \xrightarrow{\text{Homolytic fission}} \dot{A} + \dot{B}$$

or

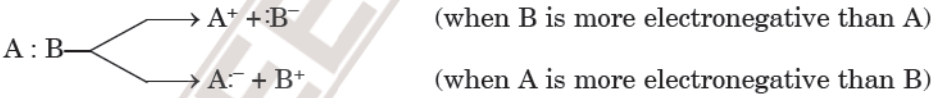
$$A \curvearrowright\!\!\!\!\!\!\curvearrowright B \longrightarrow \dot{A} + \dot{B}$$

Free radicals

Free radicals

2. Heterolytic fission

Heterolytic fission is unsymmetrical. *In this, the bond breaks in such a way that one of the fragments takes both the electrons of the shared pair leaving none on the other.* This results into two charged particles. One atom has a sextet of electrons and therefore, has a positive charge while other will have a valence octet with at least one lone pair and therefore, has a negative charge. The species that has a sextet at the carbon and is positively charged is called a **carbocation** (earlier called **carbonium ion**). The species that has a carbon atom with the shared pair of electrons and carrying a negative charge is called **carbanion.** For example,



(when B is more electronegative than A)

(when A is more electronegative than B)

The movement of electrons in organic reactions may be described by **curved arrow notation.** This shows the changes in bonding due to electronic redistribution during the reaction. The arrow starts from that point from where the electron pair is shifted and ends at a location to which electron pair moves. The following **notations** are used :

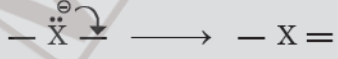
- Change in position of a pair of electrons is shown by a curved arrow starting from the electron pair which participates in the reaction.
- If the electrons being shifted belong to a bond in the reactant then the curved arrow is drawn starting from the centre of the line representing the bond.

For example,

- Shifting of electron pair from a π-bond to adjacent bond position:

- Shifting of electron pair from a π-bond to adjacent atom:

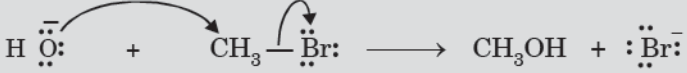
- Shifting of electron pair from atom to adjacent bond position:



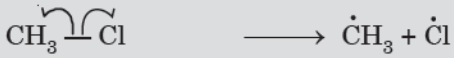
- The nonbonding electrons are shown by pair of dots on the atom.
- The movement of single electron is shown with a single barbed 'fish hooks' *i.e.,* half headed curved arrow (⟶).

In general, a ***curved arrow always means that the electron or electrons move from the atom at the tail of the arrow to the atom at the head of the arrow.***

For example, the reaction of hydroxide ion with ethyl bromide forming ethanol may be shown as :



Similarly, dissociation of chloromethane may be depicted as :



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Reaction Intermediates

The species produced during cleavage of bonds are called **reaction intermediates.** The important reaction intermediates are :

1. Free radical. *A free radical may be defined as an atom or group of atoms having an unpaired electron.* These are produced during the homolytic fission of a covalent bond.

$$A : B \xrightarrow[\text{fission}]{\text{Homolytic}} \overset{\bullet}{A} + \overset{\bullet}{B}$$

Free radicals

These free radicals are **very reactive**. This is because of the fact that they have strong tendency to pair up their unpaired electron with another electron from wherever available. These are very *short lived* and occur only as reaction intermediates during reactions. For example, dissociation of chlorine gas in the presence of ultra-violet light produces chlorine free radicals .

$$Cl : Cl \xrightarrow[\text{homolytic cleavage}]{\text{U.V.}} \overset{\bullet}{Cl} + \overset{\bullet}{Cl}$$

Chlorine free radicals

or $Cl\text{—}Cl \xrightarrow[\text{homolytic cleavage}]{h\nu} \overset{\bullet}{Cl} + \overset{\bullet}{Cl}$

The alkyl free radical may be obtained when free radical chlorine attacks methane.

$$H\text{–}\underset{H}{\overset{H}{C}}\text{:}H + \overset{\bullet}{Cl} \longrightarrow H\text{–}\underset{H}{\overset{H}{C}}\cdot + HCl$$

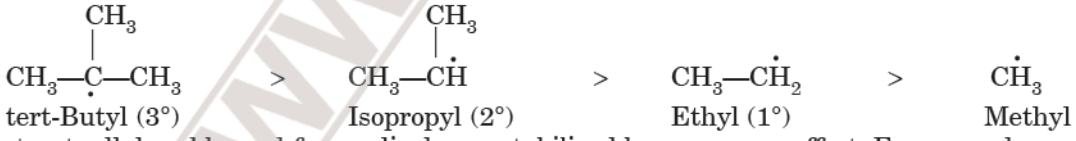
Methyl free radical

The free radicals may be classified as *primary, secondary* or *tertiary* depending upon whether one, two or three carbon atoms are attached to the carbon atom carrying the odd electron :

Stability of free radicals : The **order of stability** of alkyl free radicals is :

$$\overset{\bullet}{C}H_3 < 1° < 2° < 3°$$

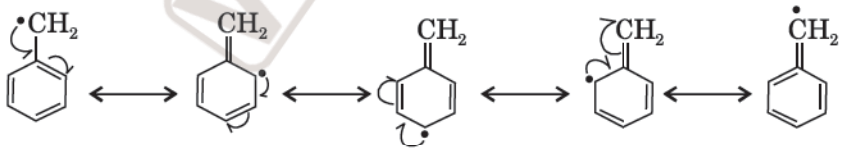
This order of stability can easily be explained on the basis of hyperconjugation. *Larger the number of alkyl groups attached to the carbon atom carrying the odd electron, greater is the delocalisation of the odd electron and hence more stable is the free radical.* Thus, the tertiary free radical with three alkyl groups attached to the carbon atom carrying the odd electron is more stable than the secondary free radical containing two alkyl groups and so on.



In contrast, allyl and benzyl free radicals are stabilized by resonance effect. For example,

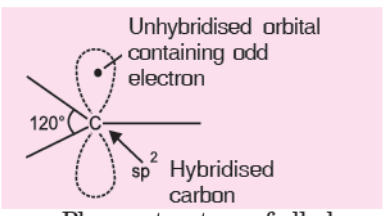
$$CH_2 = CH\text{—}\overset{\bullet}{C}H_2 \longleftrightarrow \overset{\bullet}{C}H_2\text{—}CH = CH_2$$

Allyl free radical stabilized by resonance



Benzyl free radical stabilized by resonance

Structure of alkyl free radical. The carbon atom in alkyl free radicals involves sp^2 hybridisation. Therefore, it has a **planar structure.** The three hybrid orbitals are used in the formation of three σ bonds with three H atoms or alkyl group. The unpaired electron is present in unhybridised *p*-orbital.



Planar structure of alkyl free radical

2. Carbocation. It is defined ***as a group of atoms which contain positively charged carbon atom having only six electrons (sextet of electrons) in its valence shell.*** Earlier carbocation was called **carbonium ion.** It is obtained by heterolytic fission of a covalent bond involving carbon atom.

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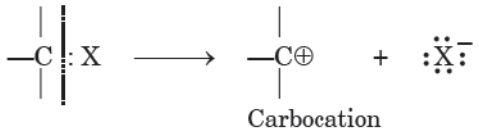
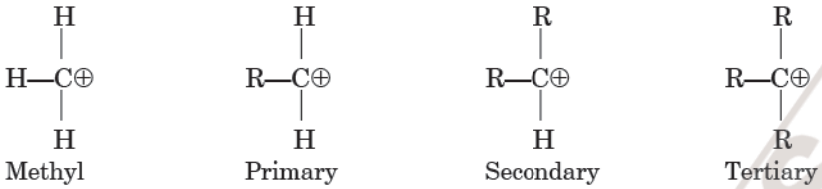


e.g., $H_3C-Br \longrightarrow H_3C^+ + Br^-$
Methyl carbocation

The carbocations are also classified as *primary* (1°), *secondary* (2°) or *tertiary* (3°) depending upon whether one, two or three carbon atoms are attached to carbon bearing the positive charge as :



Relative stability of carbocation

We know that methyl group has + I inductive effect *i.e.* electron releasing. The alkyl group attached to +vely charged carbon atom tends to release electrons towards carbon. As a result, it decreases the +ve charge on the carbon atom but itself becomes somewhat positive. As a result, the positive charge on the carbon atom gets *dispersed*. The dispersal of charge results into stability. Therefore, *more the number of alkyl groups, the greater will be the dispersal of charge and therefore, more stable will be the carbocation.*

Thus, tertiary carbocation in which there are three alkyl groups attached to positive carbon is more stable than a secondary carbocation with two alkyl groups. Similarly, a secondary carbocation is more stable than a primary carbocation which in turn is more stable than methyl carbocation :

Three alkyl groups help in dispersal of charge

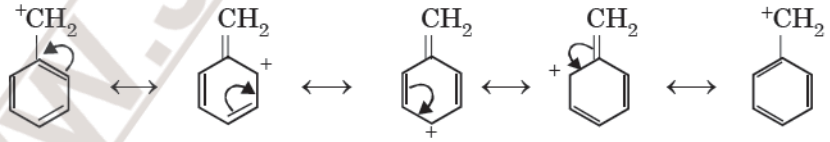
No dispersal of charge

Thus, the ***order of stability*** is :

$$3^\circ > 2^\circ > 1^\circ > CH_3^+$$

We also come across other carbocations. For example, *benzyl carbocation* is primary in nature but it is highly stable because of resonance stabilization.

Benzyl carbocation



Benzyl carbocation is stabilized by resonance

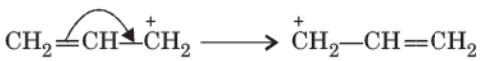
Thus, more the number of phenyl groups, greater is the stability:

$$(C_6H_5)_3C^+ > (C_6H_5)_2\,CH^+ > C_6H_5\,CH_2^+$$

Triphenyl carbocation, ***Ph_3C^+ is most stable because of resonance stabilization among three phenyl groups.***

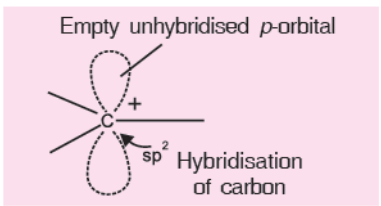
It may be noted that the presence of electron donating groups such as – CH_3, – OCH_3, –OH, etc. in the benzene ring tend to disperse the +ve charge and hence increases the stability of the carbocation. On the otherhand, the presence of electron withdrawing groups such as – NO_2, –CN, –COOH, –COOR, – Cl, etc. intensify the positive charge and hence decreases the stability of the carbocation.

Similarly, carbocations in which the + vely charged carbon atom is attached to a double bond are stabilized by resonance, For example, allyl carbocation is stabilized by resonance as :



Allyl carbocation is stabilized by resonance

Structure of carbocation. The carbon atom in carbocation is sp^2 hybridised. The three sp^2 hybrid orbitals form three σ bonds with hydrogen or other carbon atoms of alkyl groups. The unhybridised *p*-orbital of carbon remains vacant. Since it involves sp^2 hybridisation, its structure is **trigonal planar** with a bond angle of 120°.



Orbital structure of carbocation.

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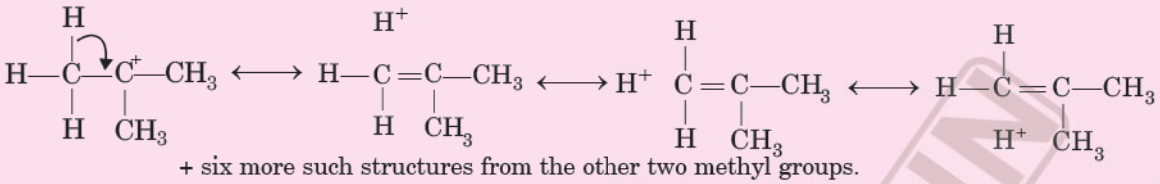
Relative stability of carbocations due to hyperconjugation effect

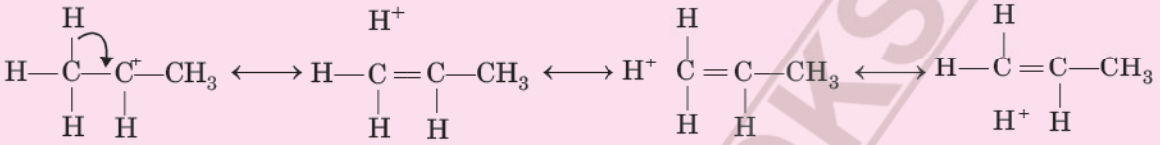
The relative stability of carbocations and free radicals follows the sequence :
tertary (3°) > secondary (2°) > primary (1°) > methyl

This order of stabilty can be easily explained on the basis of **hyperconjugation**. In case of tertiary butyl carbocation (3°), there are nine α-hydrogen atoms and hence nine hyperconjugation structures are possible :



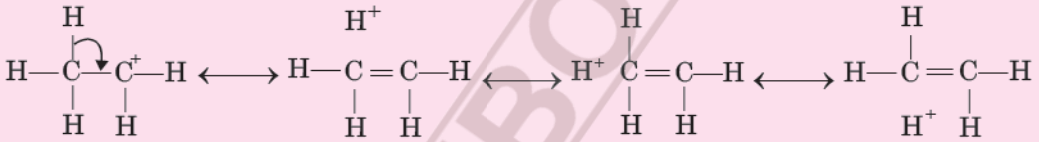
+ six more such structures from the other two methyl groups.

On the other hand, in isopropyl carbocation (2°), there are six α-hydrogen atoms and hence six hyperconjugation structures are possible :

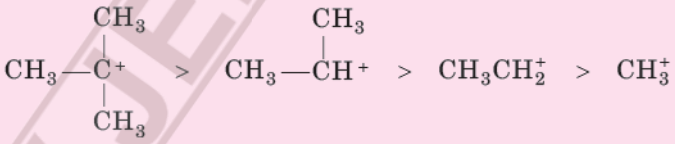


+ three more such structures from the other methyl groups.

In a similar way, ethyl carbocation (1°) has only there α-hydrogen atoms and hence only three hyperconjugation structures may be written as :



However, no hyperconjugation structure can be written for methyl, CH_3^+ carbocation. Thus, in general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, the order of stability of carbocations is



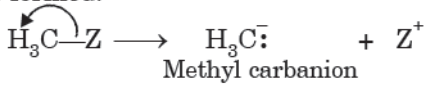
Similarly, we can explain the stability of free radicals as :

$(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$

In general, the stability of various carbocations **decreases** in the order :

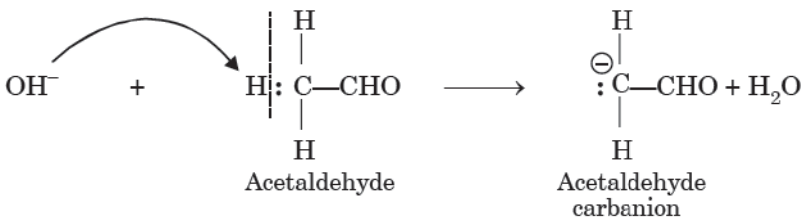
$(C_6H_5)_3C^+ > (C_6H_5)_2CH^+ > (CH_3)_3C^+ > C_6H_5CH_2^+ > (CH_3)_2CH^+ > CH_2{=}CH{-}CH_2^+ > RC^+{=}CH_2 > CH_3CH_2^+ > RCH{=}CH^+ > C_6H_5^+ > CH_3^+ > HC{\equiv}C^+$

3. Carbanion. A carbanion *may be defined as* ***a species containing a carbon atom carrying a negative charge and possessing eight electrons in its valence shell.*** These are generated by the heterolytic fission of covalent bond involving carbon atom in which the atom linked to carbon goes without the bonding electrons. As a result of this, carbon acquires a negative charge. When group Z attached to the carbon atom leaves without electron pair, the methyl carbanion is formed.



Methyl carbanion

For example, removal of hydrogen of methyl part of acetaldehyde by OH^- ions (base) leaving both the electrons on carbon :



Acetaldehyde — Acetaldehyde carbanion

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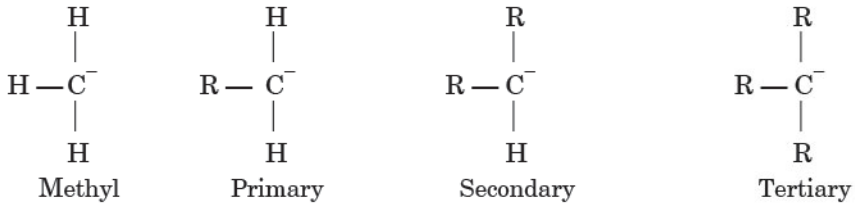
Carbanions are also very **reactive species.**

Like carbocations, carbanions are also classified as primary (1°), secondary (2°) and tertiary (3°) depending upon whether one, two or three carbon atoms are attached to the carbon atom bearing negative charge as :

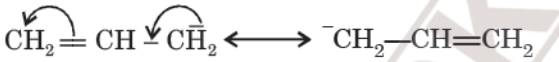


The **order of stability** of carbanions is **reverse of that of carbocations and free radicals.**

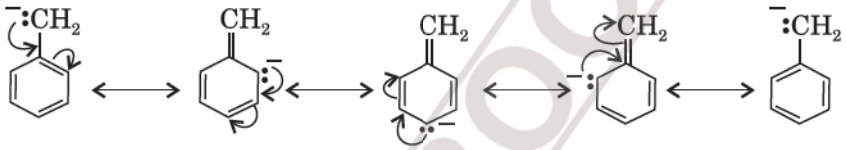
$$CH_3^- > 1° > 2° > 3°$$

This order of stability can be explained on the basis of +I, inductive effect of the alkyl group. Alkyl groups have electron releasing tendency and therefore, increase the electron density on the negatively charged carbon atom and hence make it unstable. *Larger the number of alkyl groups attached to the negatively charged carbon atom, greater will be the electron density on the carbon atom and lower will be its stability.*

It may be noted that allyl and benzyl carbanions are stabilized by resonance as :



Allyl carbanion is stabilized by resonance



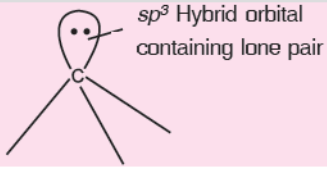
Benzyl carbanion is stabilized by resonance

Thus, more the number of phenyl groups, greater is the stability.

$$(C_6H_5)_3C^- > (C_6H_5)_2CH^- > C_6H_5CH_2^-$$

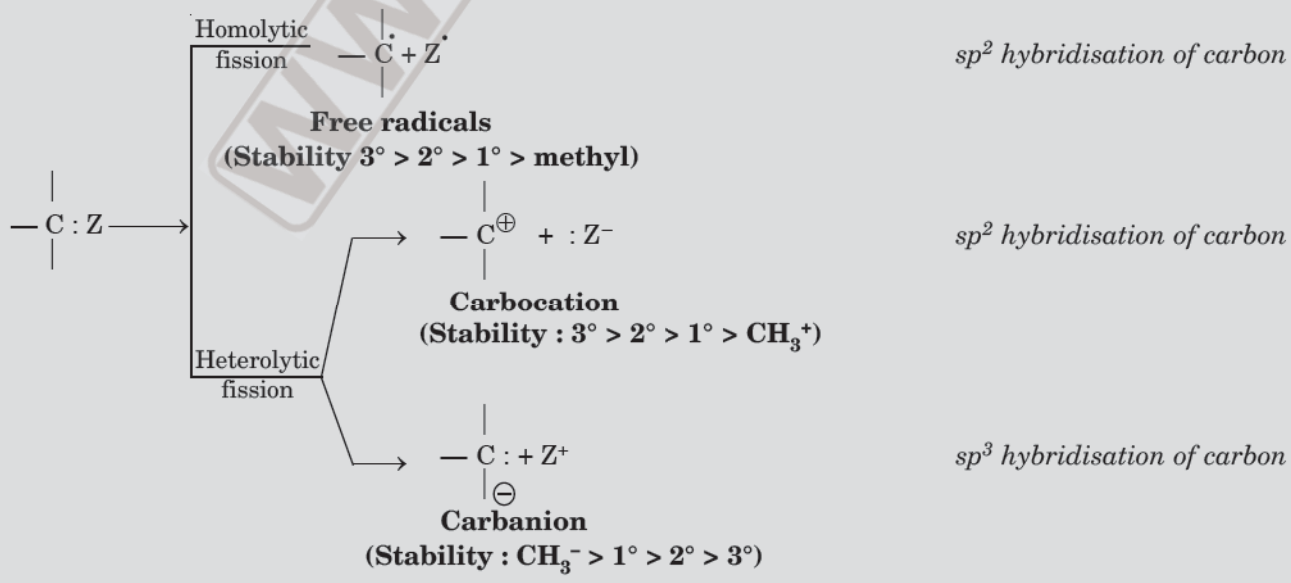
Further the presence of electron withdrawing groups such as $-NO_2$, –CN, –Cl, –COOH, –COOR, etc. in the benzene ring tend to disperse the –ve charge and hence increases the stability of the carbanion. On the other hand, the presence of electron donating groups such as $-CH_3$, $-OCH_3$, etc. tend to intensify the negative charge and hence decreases the stability of carbanion.

Structure of carbanion. The negatively charged carbon atom in carbanion is sp^3 hybridised. Therefore, it has a **tetrahedral** structure. Three of the four sp^3 hybridised orbitals form 3σ bonds with hydrogen or carbon atom of the alkyl group. The fourth sp^3 hybrid orbital contains the lone pair of electrons.



Pyramidal structure of carbanion

Thus, we may **sum up**


Homolytic fission
— C + Z
Free radicals
(Stability 3° > 2° > 1° > methyl)
sp² hybridisation of carbon
— C : Z
— C⊕ + : Z⁻
Carbocation
(Stability : 3° > 2° > 1° > CH₃⁺)
sp² hybridisation of carbon
Heterolytic fission
— C : + Z⁺
⊖
Carbanion
(Stability : CH₃⁻ > 1° > 2° > 3°)
sp³ hybridisation of carbon

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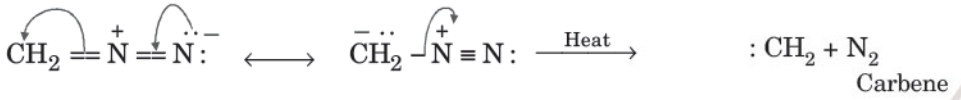
4. Carbenes. *The* **carbenes** *are reactive neutral species in which the carbon atom has six electrons in the valence shell out of which two are shared.* The simplest carbene is methylene (CH_2). It is formed when diazomethane is decomposed by the action of light.

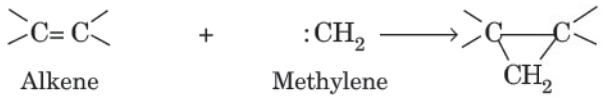
$$\underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{\text{Light}} \underset{\text{Methylene carbene}}{:CH_2} + N_2$$

This is formed as:



Carbene

It is very reactive. It reacts with alkenes by adding to the double bond forming cyclopropane.



Cyclopropane

Similarly, when chloroform is treated with sodium ethoxide, dichlorocarbene is formed.

$$CHCl_3 \xrightarrow{C_2H_5ONa} \underset{\text{Dichlorocarbene}}{:CCl_2}$$

Nitrenes

Nitrenes are the nitrogen analogues of carbenes. These are electron deficient monovalent nitrogen species. In these, nitrogen has a sextet of electrons. The parent compound is $\ddot{N}$—H (nitrene or azine) and is formed when hydrazoic acid is treated with UV light.

$$\underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow[-N_2]{h\nu} \underset{\text{Nitrene}}{H\ddot{N}:}$$

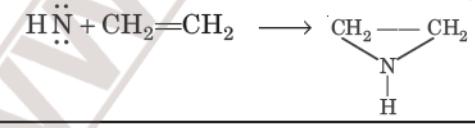
Thermal or photolytic decomposition of azides give nitrenes.

$$RN_3 \xrightarrow[\text{heat}]{h\nu} \underset{\text{Alkyl nitrene}}{R-\ddot{N}:} + N_2$$

Alkyl azide — Alkyl nitrene

This is the most common method for the generation of nitrenes.

These are very reactive species and cannot be isolated. However, nitrenes can be trapped in reactions.



TYPES OF ATTACKING REAGENTS

The attacking reagents are classified into three types :

(*i*) *Free radicals* (*ii*) *Electrophiles* (*iii*)*Nucleophiles*

1. Free radicals have already been discussed.

2. Electrophiles. A reagent that takes away an electron pair is called **electrophile**. These are *positively charged or neutral species which are deficient of electrons and can accept a pair of electrons*. These are also called *electron loving* (philic) or electron seeking species (E). These may be positively charged species or neutral molecules. For example,

H^+, H_3O^+, Cl^+, Br^+, I^+, NO^+ (nitronium ion), R^+(carbocation) (Positively charged)

$AlCl_3$, BF_3, SO_3 (Neutral)

Both Al and B have total of six electrons *i.e.*, two less than the octet. Therefore, these try to complete their octets and act as electrophiles. According to Lewis concept of acids and bases, these are called **Lewis acids.**

It may be noted that all positively charged species donot act as electrophiles. Only positively charged ions which can accept a pair of electrons can act as electrophiles. For example, Na^+, Ca^{2+}, NH_4^+ etc. cannot act as electrophiles because all have an octet of electrons in their valence shells.

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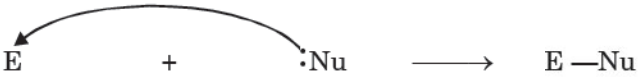
3. Nucleophiles. A reagent that brings an electron pair is called **nucleophile.** These reagents contain *an atom having unshared or lone pair of electrons.* A nucleophile is electron rich and seeks electron deficient sites, *i.e., nucleus* loving or nucleus seeking (Nu). According to Lewis concept of acids and bases, nucleophiles behave as **Lewis bases**. These may be negatively charged species or neutral molecules. For example,

H^- (hydride ion), X^-, OH^-, CN^-, R^- (carbanion), $RC{\equiv}C^-$ $RCOO^-$, OR^-, SR^-, NH_2^- (Negatively charged)

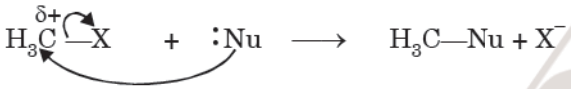
$\ddot{N}H_3$, $R\ddot{N}H_2$, $R_3\ddot{N}$, $H_2\ddot{O}:$, $R\ddot{O}H$, $R\ddot{S}R$, $R\ddot{O}R$ (Neutral molecules)

During a polar organic reaction, a nucleophile attacks an electrophilic centre which is a specific atom or part of electrophile which is electron deficient. Similarly, the electrophile attacks a nucleophilic centre, which is an electron rich specific atom or part of the nucleophile. As a result, the electrophiles get electron pair from the nucleophiles and the two form a bond. A curved-arrow notation is used to show the movement of electrons from the nucleophile to the electrophile. For example,



Electrophile Nucleophile Bond

It may be noted that in neutral molecules such as alkyl halides, the carbon is bonded to electronegative halogen atom (X). Due to the polarity of the C–X bond, carbon acquires a partial positive charge. As a result, it becomes electron deficient or electrophilic centre at which nucleophile can readily attack.



Differences between Electrophiles and Nucleophiles

	Electrophiles	Nucleophiles
1.	These are deficient in electrons.	These are rich in electrons.
2.	These accept a pair of electrons from the substrate.	These donate a pair of electrons to the substrate.
3.	These behave as Lewis acids.	These behave as Lewis bases.
4.	These have at least one empty orbital due to which they accept electrons from the substrate molecule.	These have at least one lone pair of electrons which can be easily donated to the substrate molecule.
5.	These are either neutral or positively charged chemical species.	These are neutral or negatively charged chemical species.

TYPES OF ORGANIC REACTIONS

Organic reactions can be organised broadly into two ways : by what kinds of reactions occur and by how reactions occur. These can be broadly classified into the following general types on the basis of kinds of reactions that take place.

1. Substitution reactions

The reactions in which an atom or group of atoms in a molecule is replaced or substituted by different atoms or group of atoms are called **substitution reactions.**For example, in the reaction between bromomethane with sodium hydroxide, bromine atom is replaced by hydroxide group.

$$CH_3Br + NaOH \longrightarrow CH_3OH + NaBr$$

In this reaction, a nucleophile (OH^-) substitutes the bromide in the substrate and hence this reaction is also called **nucleophilic substitution reaction.** Similarly, the substitution may take place by an electrophile or a free radical resulting *electrophilic* or *free radical substitution reactions.* For example, nitration of benzene is an example of electrophilic substitution. In this case, nitronium ion NO_2^+ acts as an electrophile. The halogenation of alkanes (e.g. methane) is an example of free radical substitution, in which free radical Cl attacks the methane molecule.

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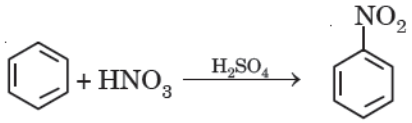
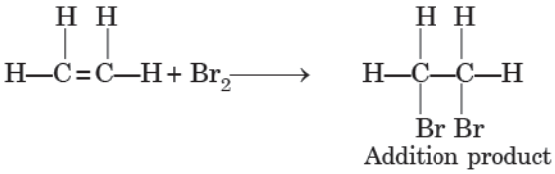
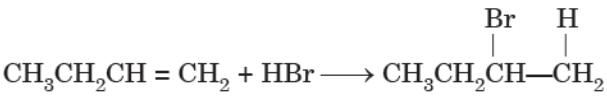
(a) 

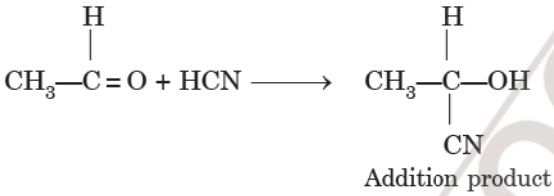
(b) $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$ (H is replaced by Cl)

2. Addition reactions

The organic reactions in which two molecules react to form a single product ***having all the atoms of the combining units*** are called **addition reactions.** For example,


Addition product

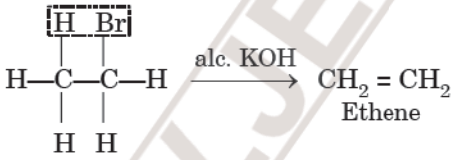



Addition product

Like substitution reactions, the addition reactions are also called free radical, electrophilic or nucleophilic addition reactions depending upon the type of attacking reagent.

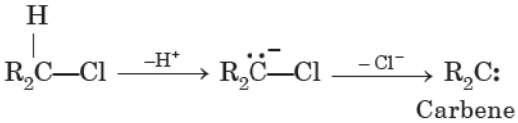
3. Elimination reactions

The reactions in which two atoms or groups of the molecule are removed are called **elimination reactions.** For example,

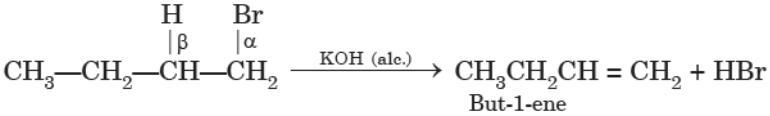

Ethene (H and Br are eliminated)

It may be noted that in these reactions, the two atoms or groups of atoms may be removed from the same or adjacent atoms of the substance. Depending upon the relative positions of the atoms or groups eliminated, these reactions are classified as α (alpha), β (beta) or γ (gamma) *elimination reactions.*

(*i*) **α-Elimination.** *In α-elimination reaction, the loss of two atoms or groups occurs from the same atom (called α-positions) of the substance.* This elimination results into electron deficient reactive intermediates, which further react to form stable products. For example, formation of carbene is an example of α-elimination reaction.


Carbene

(*ii*) **β-Elimination.** *In β-elimination reaction, the loss of two atoms or groups occurs from the adjacent positions (α, β) of the substance.* Elimination of HBr from 1-bromobutane in the presence of alcoholic KOH giving but-1-ene is an example of β-elimination reaction.


But-1-ene

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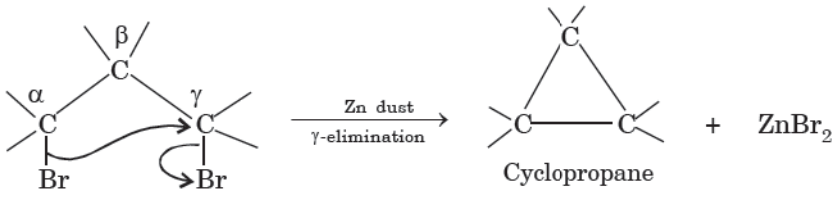
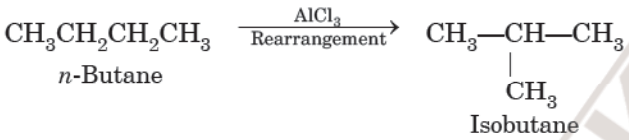
(iii) **γ-Elimination.** *In γ -elimination reaction, the loss of two atoms or groups occurs from three bonds away (next to adjacent) i.e.,* α and γ-positions. The γ-elimination results in the formation of a three membered ring as shown below :

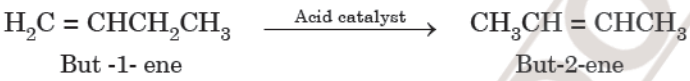


4. Rearrangement reactions

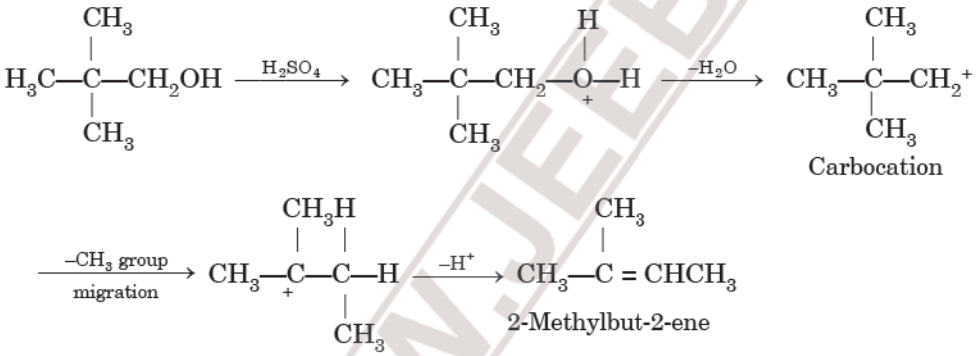
These reactions involve the migration of atoms or group of atoms to another position within the molecule under suitable conditions. For example,



Similarly, but-1-ene rearranges to but-2-ene by rearrangement in the presence of acid catalyst.

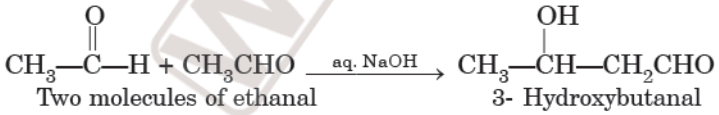


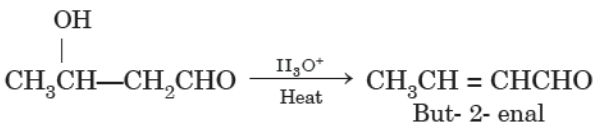
You will learn in next chapters, a typical rearrangement reaction of migration of $-CH_3$ group. Under acidic conditions, 1,2-migration of $-CH_3$ group in 2, 2-dimethylpropan-1-ol gives rearranged product 2-methyl but-2-ene as shown below :



5. Condensation reactions

In these reactions, two different or same organic reactants combine with or without the elimination of a simple molecule to give a product. For example, two molecules of acetaldehyde (CH_3CHO) condense in the presence of a base (NaOH) to form 3-hydroxybutanal. This reaction is called **aldol condensation.** The product then loses a water molecule to form but-2-enal





6. Isomerisation reactions

The reactions which involve the interconversion of isomers wherein the molecular formulae and the carbon-skeletons of reactants and products always remain same are called **isomerisation reactions.** For example,

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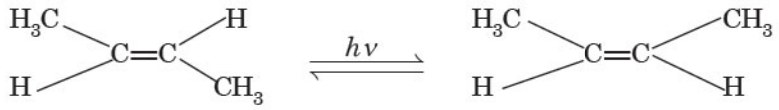
the interconversion of *trans*-but-2-ene to *cis*-but-2-ene is known as **geometrical isomerisation reaction.**

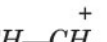


trans-But-2 ene *cis*-But-2-ene

SOLVED EXAMPLES

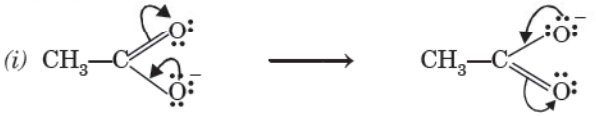
Example 21.

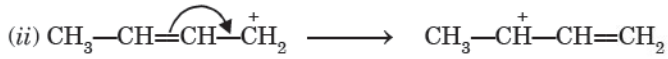
Write resonance structures of the following showing the movement of electrons by curved arrows :
(i) Acetate ion, CH_3COO^-

(ii) 

N.C.E.R.T.

Solution :

(i) 

(ii) 

Example 22.

Give reasons why the following two structures I and II cannot be the major contributors to the real structues of CH_3COOCH_3.

N.C.E.R.T.

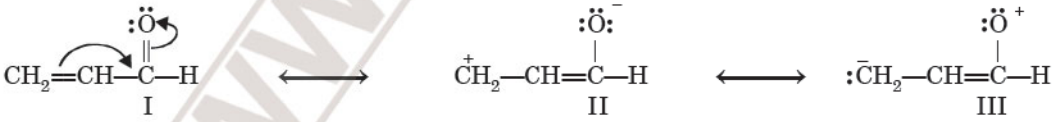
I *II*

Solution : The structures I and II are less important contributors because they involve 'charge separation'. Therefore, they donot contribute substantially towards the resonance hybrid. Further, structure I also contains a carbon atom with an incomplete octet (sextet of electrons) and therefore, its contribution is lower than that of structure II.

Example 23.

Write resonating structures for CH_2 = CHCHO. Indicate relative stability of the contributing structures :
Solution : The resonating structures for CH_2 = CHCHO are :

N.C.E.R.T.

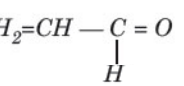
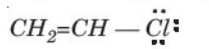


I II III

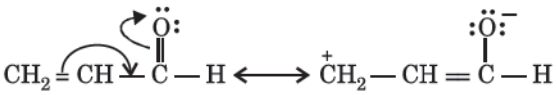
Structure I is most stable because it has more number of covalent bonds and each carbon and oxygen atoms has an octet and no carbon or oxygen atom has a charge. Structure III is least stable because more electronegative O atom has positive charge and electropositive carbon has negative charge. In structure II, there is positive charge on electropositive C atom and negative charge on electronegtive O atom. But both structures II and III have charge separation. Thus, decreasing order of stability is : I > II > III

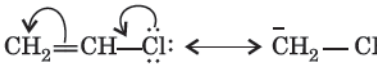
Example 24.

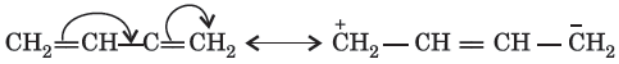
Draw resonance structures for the following compounds :

(i)  *(ii)*  *(iii)*

N.C.E.R.T.

Solution : *(i)* 

(ii) 

(iii) 

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❑ **Example 25.** N.C.E.R.T.

Classify the following molecules/ions as nucleophiles or electrophiles :

HS^-, BF_3, $CH_3CH_2O^-$, $(CH_3)_3N$, Cl^+, $CH_3C = O$, H_2N^-:, NO_2^+

Solution : Electrophiles : BF_3, Cl^+, $CH_3C^+{=}O$, NO_2^+

In these, the reactive sites have only six valence electrons and therefore can accept electron pairs from a nucleophile.

Nucleophiles : HS^-, $CH_3CH_2O^-$, $(CH_3)_3N$, $H_2N{:}^-$

These species have unshared pair of electrons which can be donated and shared with an electrophile.

❑ **Example 26.**

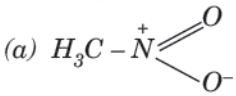
Identify the electrophilic centre in the following : (i) CH_3CN (ii) H_3CI (iii) CH_3CHO

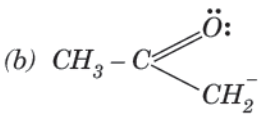
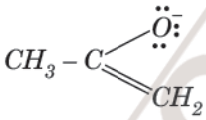
Solution : The electrophilic centres are shown by starred carbon (C*) because these will acquire partial positive charge due to the polarity of the bond :

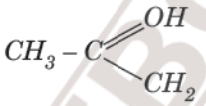
(*i*) $H_3CC^*{\equiv}N$ (*ii*) $H_3C^*{-}I$ (*iii*) $CH_3HC^*{=}O$

❑ **Example 27.**

Which of the following pairs of structures do not constitute resonance structures :

(*a*)  and $H_3C - O - N = O$

(*b*)  and 

(*c*) $(CH_3)_2CO$ and 

(*d*) $CH_3CH{=}CHCH_3$ and $CH_3CH_2CH{=}CH_2$

Solution :

(*a*) The two structures differ in the position of atoms and therefore, do not constitute resonance structures.

(*b*) These constitutes a pair of resonance structures.

(*c*) Thes are not resonance structures because these differ in the position of atoms

(*d*) These are not resonance structures because these differ in the position of atoms.

❑ **Example 28.** N.C.E.R.T.

Using curved arrows notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage :

(a) CH_3—SCH_3 (b) CH_3—CN (c) CH_3—Cu

Solution :

(*a*) $CH_3{-}\overset{+}{S}CH_3 \longrightarrow \overset{+}{C}H_3 + \overset{-}{S}CH_3$

(*b*) $CH_3{-}\overset{+}{C}N \longrightarrow \overset{+}{C}H_3 + \overset{-}{C}N$

(CN is more electronegative than CH_3)

(*c*) $\overset{-}{C}H_3{-}\overset{+}{C}u \longrightarrow \overset{-}{C}H_3 + \overset{+}{C}u$

(Cu is more electropositive than CH_3)

❑ **Example 29.** N.C.E.R.T.

Classify the following reactions according to the reaction type :

(*a*) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$

(*b*) $(CH_3)_2C = CH_2 + HCl \longrightarrow (CH_3)_2C(Cl){-}CH_3$

(*c*) $CH_3CH_2Br + HO^- \longrightarrow CH_2 = CH_2$

(*d*) $H_2C = CHCH_2CH_3 \longrightarrow H_3C\,CH = CHCH_3$

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(e) $CH_3—\underset{\displaystyle C_6H_5}{\underset{|}{C}} = NOH \longrightarrow CH_3—\underset{\displaystyle NHC_6H_5}{\underset{|}{C}} = O$

(f) $(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_2C = CH_2 + H_2O + Cl^-$

(g) $(CH_3)_3C—CH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$ **N.C.E.R.T.**

Solution :

(a)	$CH_3CH_2Br + HO^-$	$\longrightarrow$ $CH_3CH_2SH + Br^-$	Substitution reaction
(b)	$(CH_3)_2C = CH_2 + HS^-$	$\longrightarrow$ $(CH_3)_2C(Cl)—CH_3$	Addition reaction
(c)	$CH_3CH_2Br + OH^-$	$\longrightarrow$ $CH_2 = CH_2$	Elimination reaction
(d)	$H_2C = CHCH_2CH_3$	$\longrightarrow$ $H_3C\,CH = CHCH_3$	Isomerisation reaction
(e)	$CH_3\underset{\displaystyle C_6H_5}{\underset{|}{C}} = NOH$	$\longrightarrow$ $CH_3—\underset{\displaystyle NHC_6H_5}{\underset{|}{C}} = O$	Rearrangement reaction
(f)	$(CH_3)_3CCl + OH^-$	$\longrightarrow$ $(CH_3)_2C = CH_2 + H_2O + Cl^-$	Elimination reaction.
(g)	$(CH_3)_3C—CH_2OH + HBr$	$\longrightarrow$ $(CH_3)_2CBrCH_2CH_3 + H_2O$	Substitution with rearrangement reaction

❑ Example 30.

Classify the reagents shown in bold in the following equations as nucleophiles or electrophiles :

(a) $CH_3COOH + \mathbf{HO^-} \longrightarrow CH_3COO^- + H_2O$

(b) $CH_3CH_2Br + \mathbf{HS^-} \longrightarrow CH_3CH_2SH + Br^-$

(c) $C_6H_6 + \mathbf{CH_3CO^+} \longrightarrow C_6H_5COCH_3$

(d) $CH_3COCH_3 + \mathbf{CN^-} \longrightarrow CH_3\underset{\displaystyle CN}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}—CH_3$

Solution :

(a) $CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—OH + HO^- \longrightarrow CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—O^- + H_2O$

OH^- is nucleophile

(b) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$

SH^- is nucleophile

(c) $C_6H_6 + CH_3CO^+ \longrightarrow C_6H_5COCH_3$

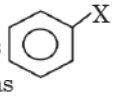
CH_3CO^+ acts as electrophile

(d) $CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3 + CN^- \longrightarrow CH_3—\underset{\displaystyle CN}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}—CH_3$

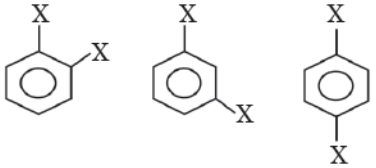
CN^- is nucleophile

add on Conceptual Questions 1

Q.1. How many isomers are possible for monosubstituted and disubstituted benzene ?

Ans. There is one monosubstituted benzene as 

There are three disubstituted benzenes as



ortho (1, 2-) *meta (1,3-)* *para(1,4-)*

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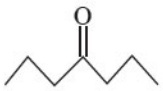
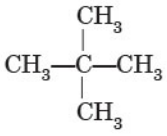
CONCEPTUAL QA

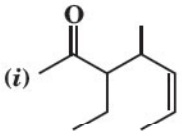
Q.2. Write bond line formula for heptan-4-one.

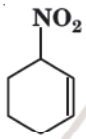
Ans. 

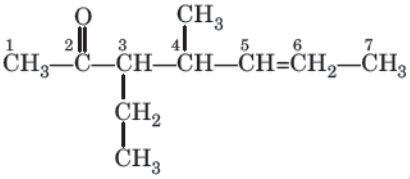
Q.3. Give the IUPAC name of the alkane having the lowest molecular mass that contain a quaternary carbon.

Ans.  2, 2- Dimethylpropane

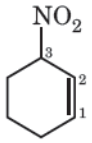
Q.4. Name the following compounds :

(*i*) 

(*ii*) 

Ans. (*i*) 

3-Ethyl-4-methylhept-5-en-2-one

(*ii*)  : 3-Nitrocyclohex-1-ene

Q.5. Write structural formulae for the following :

(*i*) 1-Bromoheptane (*ii*) 5-Bromoheptanoic acid

Ans. (*i*) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2Br$

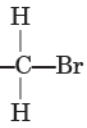
(*ii*) $CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_2 - CH_2 - CH_2 - COOH$

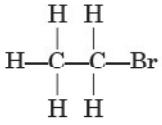
Q.6. Which of the following compounds shows geometrical isomerism ?

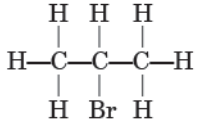
(i) Pent-1-ene (ii) 2-Methylbut-2-ene (iii) Pent-2-ene

Ans. Pent-2-ene

Q.7. Draw the complete structures of bromomethane, bromoethane, 2-bromopropane and *tert*-butyl bromide. Arrange them in order of increasing steric hindrance. ***N.C.E.R.T.***

Ans. (*i*) Bromomethane, CH_3Br : 

(*ii*) Bromoethane, CH_3CH_2Br : 

(*iii*) 2-Bromopropane, $CH_3CHBrCH_3$: 

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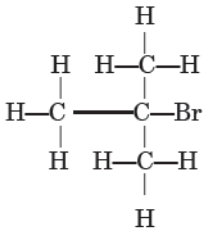
(iv) tert-Butyl bromide, $(CH_3)_3CBr$:



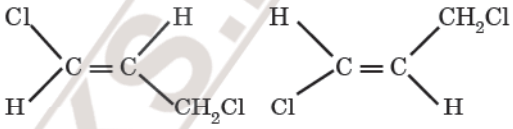
Increasing order of steric hindrance :

Bromomethane < Bromoethane < 2-Bromopropane < tert-Butyl bromide.

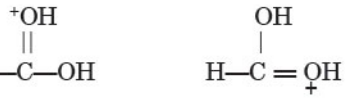
Q.8. What is the relationship between the members of the following pairs of structures ? Are they identical, structural, geometrical or resonance contributors ?

(i)

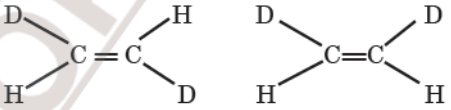
(ii)



(iii)



(iv)



Ans. *(i)* Structural isomers

(ii) Identical

(iii) Resonance contributors

(iv) Geometrical isomers.

Q.9. How many tetrahedral angles does a molecule of methane have?

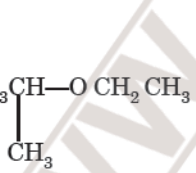
Ans. Six tetrahedral angles.

Q.10. Draw structures of all isomeric ethers corresponding to molecular formula $C_5H_{12}O$.

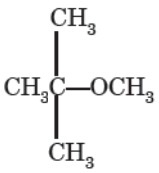
Ans. The isomeric ethers for $C_5H_{12}O$ are :

(i) $CH_3CH_2CH_2CH_2OCH_3$ *(ii)* $CH_3CH_2CH_2OCH_2CH_3$

(iii)



(iv)



Q.11. What is the hybridisation of each carbon in $CH_2 = C = CH_2$?

Ans. sp^2, sp and sp^2.

Q.12. Show the polarisation of carbon-magnesium bond in the following structure : ***N.C.E.R.T.***

CH_3CH_2—CH_2MgX.

Ans. $CH_3CH_2\overset{\delta-}{C}H_2—\overset{\delta+}{M}g—X$

Q.13. What type of strurctural isomerism is shown by

CH_3—S—$CH_2CH_2CH_3$ and **CH_3—S—CH(** **)**

Ans. Metamerism.

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Q.14. How many cyclic and acyclic isomers are possible for the molecular formula C_3H_6O? Draw these.

Ans. Seven isomers are possible. These are :

(*a*) *Acyclic isomers :*

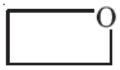
(*i*) CH_3CH_2CHO Propanal

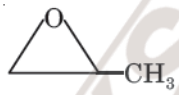
(*ii*) $CH_3\overset{\overset{O}{\|}}{C}CH_3$ Propanone

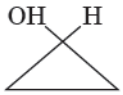
(*iii*) $CH_2 = CHCH_2OH$ Prop-2-en-1-ol

(*iv*) $CH_2 = CHOCH_3$ Methoxyethene

(*b*) *Cyclic isomers :*

(*v*)  Oxetane

(*vi*)  Propylidene oxide

(*vii*)  Cyclopropanol

CONCEPTUAL QA

Q.15. In which C—C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be least ?

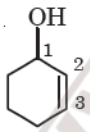
Ans. The inductive effect is least in C_2—C_3 bond because the magnitude of inductive effect decreases as the number of intervening bonds increases.

$\overset{3}{C}H_3—\overset{2}{C}H_2—\overset{1}{C}H_2—Br$

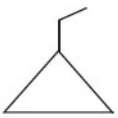
Q.16. Draw the structures of

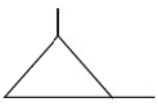
***(i)* Pent–4–en–2–ol** ***(ii)* Cyclohex–2–en–1–ol**

Ans. (*i*) $\overset{5}{C}H_2 = \overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H(OH)\overset{1}{C}H_3$

(*ii*) 

Q.17. Draw polygon formulae for the molecular formula C_5H_{10}.

Ans. (*i*) (*ii*) (*iii*) 

(*iv*) (*v*) 

Q. 18. What is the type of hybridisation of each carbon in the following compounds : ***N.C.E.R.T.***

(i) $CH_3CH = CHCN$ ***(ii)*** $(CH_3)_2C = O$

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Ans. *(i)* $\overset{sp^3}{CH_3}—\overset{sp^2}{CH}=\overset{sp^2}{CH}—\overset{sp}{C}\equiv N$: sp^3, sp^2, sp^2, sp

(ii) $\overset{sp^3}{CH_3}—\overset{sp^2}{C}(=O)(CH_3)$: sp^3, sp^2, sp^3

Q. 19. Which bond is more polar in the following pairs of molecules :

(i) **$H_3C—H$ or $H_3C—Br$** ***(ii)*** **$H_3C—NH_2$ or $H_3C—OH$**

(iii) **$H_3C—OH$ or $H_3C—SH$**

N.C.E.R.T.

Ans. *(i)* C—Br because Br is more electronegative than H.

(ii) C–O because O is more electronegative than N.

(iii) C—O because O is more electronegative than S.

Q. 20. Which is expected to be more stable :

$O_2N\ CH_2\ CH_2O^-$ and $CH_3CH_2O^-$ and why ?

Ans. $O_2NCH_2CH_2O^-$ is more stable than $CH_3CH_2O^-$ because $-NO_2$ group has –I inductive effect and tends to disperse the –ve charge on the O-atom. This results into stability. However, CH_3CH_2 – group has + I effect and tends to intensify the –ve charge and therefore, destabilizes it.

Q.21. Write structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.

Ans. $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

The possible carbocations are :

$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\overset{+}{C}H_2$ (I (1°)) $\quad$ $CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}H—\overset{+}{C}HCH_3$ (II (2°)) $\quad$ $CH_3—\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}—CH_2—CH_3$ (III (3°)) $\quad$ $\overset{+}{C}H_2—\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$ (IV (1°))

Order of increasing stability I < IV < II < III.

Q.22. Identity the most stable species in the following sets of ions giving reasons :

(a) **$\bar{C}H_3$, $\bar{C}H_2Cl$, $\bar{C}HCl_2$, $\bar{C}Cl_3$**

(b) **$\overset{+}{C}H_3$, $\overset{+}{C}H_2Br$, $\overset{+}{C}HBr_2$, $\overset{+}{C}Br_3$**

Ans. *(a)* $\bar{C}$–Cl_3 is most stable because Cl is more electronegative than hydrogen. On replacing hydrogen by chlorine, negative charge on C is reduced and the species becomes stable.

(b) $\overset{+}{C}H_3$ is most stable. The replacement of H by Br increases positive charge on carbon atom because Br is more electronegative than H and consequently the species becomes less stable.

Q.23. Which of the following resonance structure for propenal is more stable ?

Ans. $\underset{\text{(A)}}{CH_2=CH-CH=O} \longleftrightarrow \underset{\text{(B)}}{\overset{+}{C}H_2-CH=CH-\bar{O}}$

A is more stable than B.

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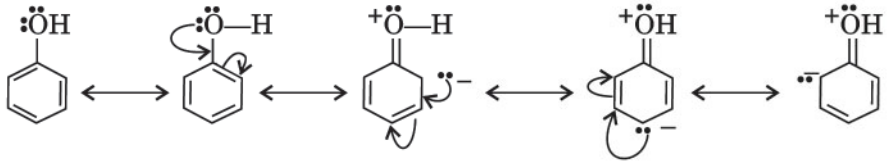
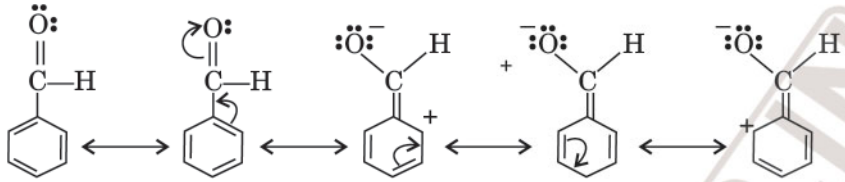
Q. 24. Draw resonance structures for the following

(*i*) C_6H_5OH (*ii*) C_6H_5CHO (*iii*) $C_6H_5—CH_2^+$

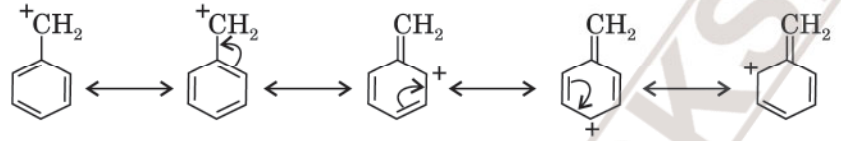
Ans (*i*)



(*ii*)



(*iii*)



CONCEPTUAL QA

Q.25. List the following carbocations in the order of decreasing stability :

$CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_2^+$, $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2^+$, $CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_2^+$

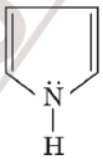
Ans. $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2^+ > CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_2^+ > CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_2^+$

Q.26. Explain why $(CH_3)_3C^+$ is more stable than $CH_3CH_2^+$ and CH_3^+ is the least stable cation.

Ans. Hyperconjugation interaction in carbocations depends upon the number of α-hydrogen atoms. It is greater in $(CH_3)_3C^+$ than in $(CH_3)_2CH^+$ because $(CH_3)_3C^+$ has nine C—H bonds while $(CH_3)_2CH^+$ has only six C—H bonds. Greater hyperconjugation means greater stability of the cation and hence $(CH_3)_3C^+$ is more stable than $(CH_3)_2CH^+$. In CH_3^+, the vacant *p*-orbital is perpendicular to the plane in which C—H bonds lie and hence there is no possibility of overlapping. Thus CH_3^+ lacks hyperconjugation stability and is the least stable carbocation.

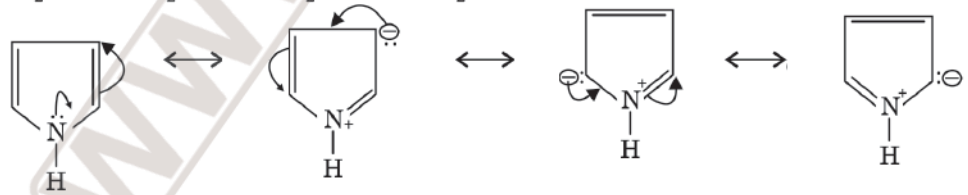
Q.27. Write resonance structures of

(*i*) allyl carbocation **(*ii*)**



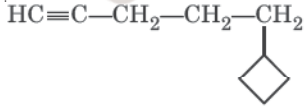
Ans. (*i*) $CH_2=CH—CH_2^+ \longleftrightarrow CH_2^+—CH=CH_2$

(*ii*)

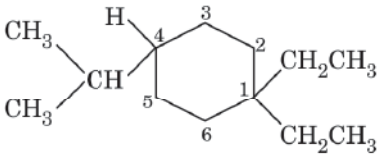


Q.28. Write IUPAC name of the following :

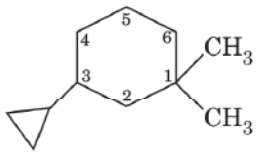
(*i*)



(*ii*)



(*iii*)



Ans. (*i*) 5-Cyclobutylpent-1-yne (*ii*) 1,1-Diethyl-4-isopropylcyclohexane
(*iii*) 3-Cyclopropyl-1,1-dimethylcyclohexane

Q.29. Arrange the following free radicals in decreasing order of stability :

$\dot{C}H_3$, $(CH_3)\dot{C}$, $CH_3\dot{C}H_2$, $-\dot{C}H_2$, $CH_2=CH—\dot{C}H_2$, $(CH_3)_2\dot{C}H$

Ans. $-\dot{C}H_2 > CH_2=CH—\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

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PURIFICATION OF ORGANIC COMPOUNDS

The organic compounds extracted from the natural sources or prepared in the laboratory are generally impure and therefore, it is necessary to first purify them and check their purity. The various methods used for purification are based on the nature of the compound and the impurities present in it.

The most common methods used for the purification of organic compounds are :

1. *Filtration*
2. *Recrystallisation*
3. *Sublimation*
4. *Distillation*
5. *Fractional distillation*
6. *Distillation under reduced pressure*
7. *Steam distillation*
8. *Differential extraction*
9. *Chromatography.*

After purifying the compounds, it is necessary to check their purity. The most convenient and commonly used physical properties to test the purity of a substance in the laboratory are melting points for solids and boiling points for liquids. Most of the pure compounds have sharp melting and boiling points. Nowadays, the purity of an organic compound is determined by new methods based on different types of chromatographic and spectroscopic techniques.

Let us briefly learn about different methods for purifying the organic compounds.

1. Filtration

The process of filtration is used to separate an insoluble solid component of the mixture from the soluble component in a given solvent.

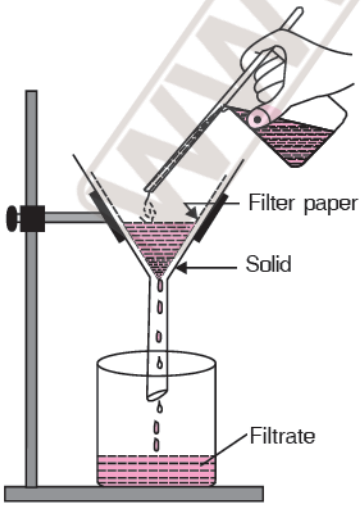

Fig. 6. Process of filtration.

This process is carried out with the help of a *filter paper* which is placed in the funnel. The mixture is dissolved in a suitable solvent in which one component dissolves. It is then slowly allowed to fall on the funnel as shown in Fig. 6. The liquid containing soluble component passes through the filter paper and the insoluble solid is retained on the filter paper.

For example, **a mixture containing naphthalene and urea** can be separated by this technique. Urea dissolves in water while naphthalene remains insoluble. The residue on the filter paper is naphthalene while urea is in the solution (filtrate). Urea is recovered from the filtrate by evaporating water.

Sometimes the filtration is carried out in a fluted filter paper placed in a glass funnel (Fig. 7). The use of the fluted filter paper makes the filtration rapid.

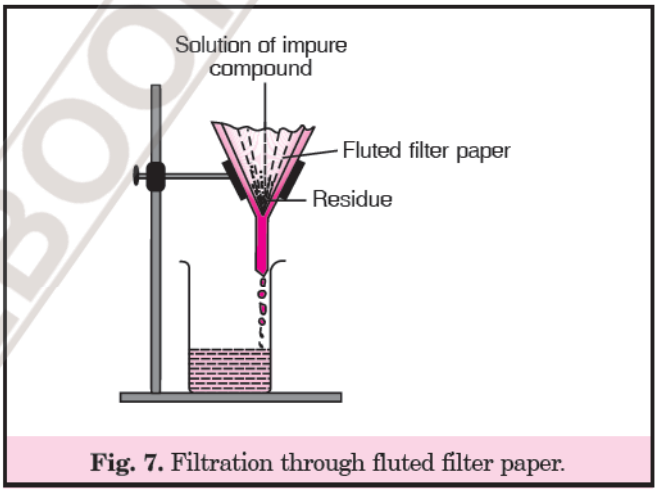

Fig. 7. Filtration through fluted filter paper.

If the filtration of a hot solution is required, it is carried out in a *hot water funnel*. This is used when the organic compound crystallises during filtration (Fig. 8). The jacket of the hot water funnel is heated from outside and this keeps the solution hot in the glass funnel. This will prevent the formation of crystals during filtration. The insoluble and suspended impurities remain on the filter paper and a clear solution gets collected in the beaker placed below the funnel. For example, **a mixture of anthracene and benzoic acid** is separated by dissolving it in hot water and filtering the hot solution. Anthracene remains as an insoluble residue while benzoic acid goes in the filtrate. It crystallizes on cooling.

At times, the process of filtration is very slow and takes a long time. In such cases, the filtration is carried out under reduced pressure using *Buckner funnel* and a water suction pump as shown in Fig. 9. The suction pump enables the filtration under reduced pressure and is, therefore, quite fast.

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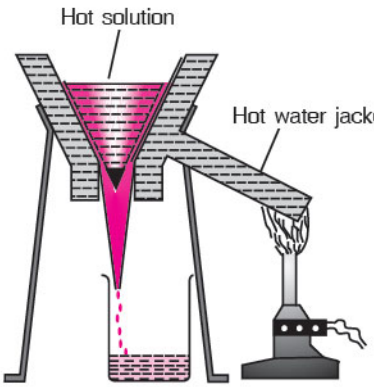

Fig. 8. Filtration through hot water funnel.

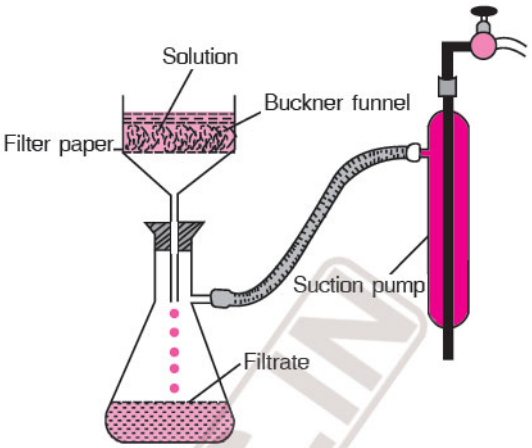

Fig. 9. Filtration under reduced pressure.

2. Recrystallisation

This is the most common method for purifying organic solids. This method is based *on the differences in the solubility of the organic compound and its impurities in a suitable solvent*. This method involves the following steps :

(*a*) Preparation of the solution. The given organic substance is powdered and is dissolved in a suitable solvent by heating. The amount of solvent should be just sufficient to dissolve the whole of the solid on heating. In case of solvents with low boiling points, the heating must be done carefully by using either an air condenser or water condenser, so that the vapour of the solvent may not come in contact with the flame.

Choice of solvent. The choice of solvent is very important in the crystallisation process. The main conditions of the solvent are :

(*i*) *The organic substance should be sparingly soluble at room temperature but appreciably soluble at higher temperature.*
(*ii*) *The solvent should crystallise on cooling.*
(*iii*) *The solvent should not dissolve the impurities.*
(*iv*) *The solvent should not react chemically with the substance.*
(*v*) *Removal of solvent becomes easy if it is low boiling liquid.*

The choice of a solvent is very crucial. For example, suppose we want to purify **sugar containing an impurity of common salt**. This can be done by treating the mixture with ethanol around 350 K. The sugar will dissolve whereas common salt remains insoluble. The filtrate on cooling will give crystals of sugar. In this case, we cannot take water as the solvent because both sugar and common salt are soluble in water.

(*b*) Filtration of the solution. The hot saturated solution [prepared in step (*a*)] is filtered preferably through a fluted filter paper placed in a glass funnel as described earlier. If the organic compound crystallises during filtration, then *a hot water funnel* is employed for filtration (Fig. 8). The jacket of the hot water funnel is heated from outside and this keeps the solution hot in the glass funnel.

(*c*) Crystallisation. The hot filtrate is allowed to cool *slowly* and *undisturbed* in a beaker or in a crystallising dish. After some time the crystals of the pure compound are formed. Sometimes, the sides of the vessel are scratched. This helps the process of crystallisation.

(*d*) Separation of crystals. The crystals formed (step c) are separated from the mother liquor by filtration. The filtration is normally done by use of *Buckner funnel* and a suction pump (Fig. 9). This enables the filtration under reduced pressure and is, therefore, quite fast. The crystals are washed 2-3 times with small quantities of pure solvent.

(*e*) Drying of crystals. The crystals are dried by pressing between the folds of filter paper and then placed in a steam or air oven for some time. The crystals are finally dried over sulphuric acid or calcium chloride in a desiccator.

(*f*) Removal of colour. Sometimes the crystals obtained are slightly coloured due to the presence of some coloured impurities. In such cases, the crystals are redissolved in the same solvent and a pinch of **animal charcoal** is added. The solution is boiled and then filtered as before. The charcoal adsorbs all the coloured impurities and the crystals now obtained are colourless.

If the substance contains impurities of comparable solubilities, it can be purified by repeated crystallisation.

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3. Sublimation

Certain organic solids on heating directly change from solid to vapour state without passing through a liquid state. Such substances are called sublimable. This process is called *sublimation*. The vapours on cooling change back to the solid form.

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapours}$$

The sublimation process is used for the separation of sublimable volatile compounds from non-sublimable impurities.

In this process, the impure solid is taken in a porcelain dish and covered with a perforated filter paper. An inverted funnel is placed over it. The stem of the funnel is plugged with a little cotton and the sides are kept cooled (Fig. 10).

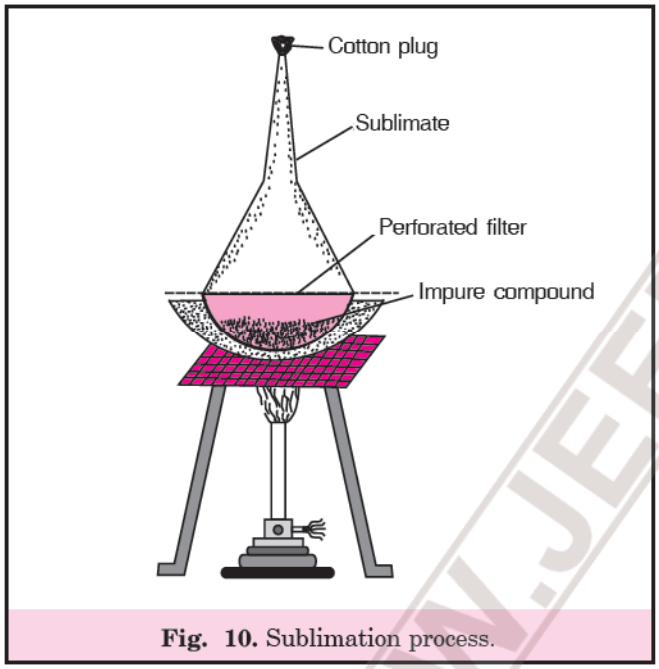

Fig. 10. Sublimation process.

The dish is heated gently over sand bath when the substance volatilises and gets collected on the inner cold surface of the inverted funnel. The non-volatile impurities are left in the dish. The perforated filter paper allows the vapours to go up but checks the sublimate from falling back to the dish.

The process is generally used for the purification of ***camphor, naphthalene, anthracene, benzoic acid,*** etc. containing non-volatile impurities.

4. Distillation

This method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. The simple distillation involves the heating of the liquid to its boiling point so that it is converted into vapours. On cooling the vapours, pure liquid is obtained and collected separately.

The apparatus employed for the process is shown in Fig. 11. It consists of a distillation flask having a side tube connected to a *Leibig's condenser*. The liquid to be purified is taken in the distillation flask. A few unglazed porcelain pieces or glass beads are added to the liquid to avoid bumping. The flask is gently heated on a water bath or oil bath or even directly, depending upon the boiling point of the liquid. When heating is continued, the liquid starts boiling at a constant temperature and almost whole of it has changed into vapours. When it passes through the condenser, the vapours get condensed to the liquid form. The pure liquid is collected in the receiver kept at the open end of the condenser. *The distillate contains pure liquid while the impurities are left behind in the distillation flask.*

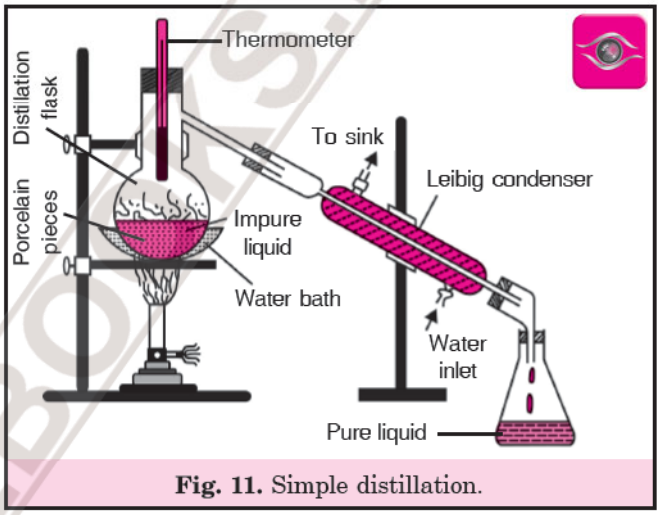

Fig. 11. Simple distillation.

This method can also be used for separating liquids having sufficient difference in their boiling points. The liquids having different boiling points vapourize at different temperatures. The vapours are cooled and the liquids so formed are collected separately. The liquid mixture is taken in a round bottom flask and heated carefully in an apparatus as shown in Fig. 11. The liquid having lower boiling point will vapourize first and its vapours are condensed using a condenser and the liquid formed is collected. The vapours of higher boiling component form later and condensed separately.

Thus, the **object of simple distillation** is to

- separate volatile liquids from non-volatile impurities.
- separate liquids having sufficient difference in their boiling points.

This method can be used to separate a mixture of

(i) chloroform (b.p. 334 K) and aniline (b.p. 457 K)

(ii) ether (b.p. 308 K) and toluene (b.p. 384 K)

(iii) benzene (b.p. 353 K) and aniline (b.p. 457 K)

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5. Fractional Distillation

This process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. In these cases, the process of simple distillation will fail because the vapours of both the liquids will be formed simultaneously and the distillate will also contain both of them. To solve the problem, the distillation is carried out by using fractionating columns. The *fractionating column* is a long tube *provided with obstructions to the passage of the vapours moving upwards and liquid moving downwards*. It is a long glass tube with a wide bore packed with glass beads or porcelain rings or blown into a number of spherical or pear shaped bulbs. Because of the obstructions, the fractionating column increases the cooling surface area. The common types of fractionating columns are shown in Fig. 12. The fractionating column is fitted to the distillation flask.

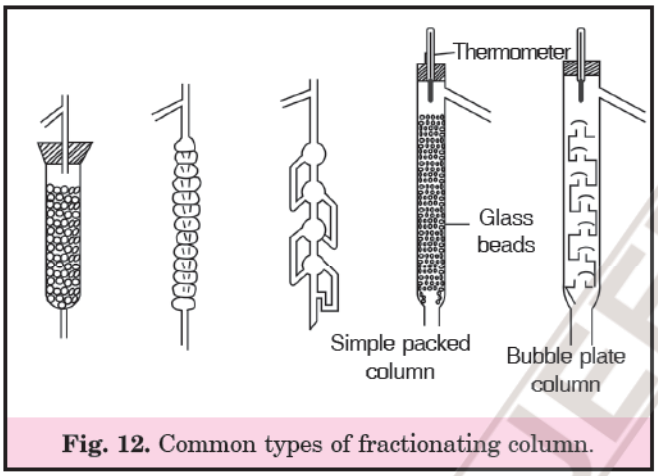

Fig. 12. Common types of fractionating column.

Purpose of Fractionating Column. The fractionating column provides more surfaces for heat exchanges and obstructions to the ascending vapours and the descending liquid. When the flask is heated, the vapours of more volatile liquid (low boiling component) rise up in the fractionating column. Due to the obstructions in the fractionating column, some of the vapours condense and fall back in the column. Some of the condensing liquid in the fractionating column gets heat from the ascending vapours and revaporizes. As a result, the vapours become richer in low boiling component. These rise up in the fractionating column and condense while passing through the condenser. They are collected in the receiver.

The vapours of the less volatile liquid (high boiling component) also rise into the column but due to many obstructions they get condensed in the column and flow back to the distillation flask. After a series of successive distillations, the remaining liquid in the distillation flask gets richer in higher boiling component. Therefore, the receiver contains the fraction rich in more volatile liquid. The process may be repeated to get pure liquids. Each successive condensation and vaporisation is called **theoretical plate.** These days commercially, columns with hundreds of plates are available. This method may be used to **separate a mixture of acetone (b.p. 330 K) and methyl alcohol (b.p. 338 K).**

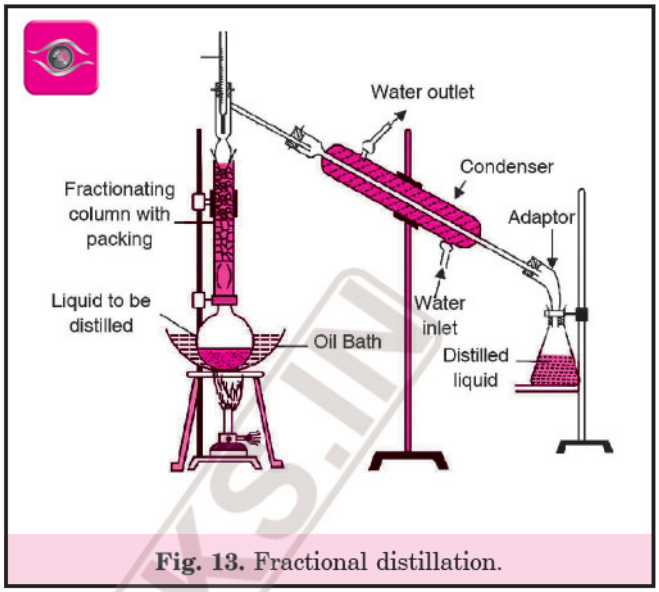

Fig. 13. Fractional distillation.

One of the technological applications of fractional distillation is to **separate different fractions of crude oil in petroleum industry.**

6. Distillation under Reduced Pressure : Vacuum Distillation

Certain liquids have a tendency to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation. Therefore, *vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.* Under reduced pressure, the liquid will boil at a low temperature and the temperature of decomposition will not be reached. For example, *glycerol boils with decomposition at 563 K but if the pressure is reduced to 12 mm, it boils at 453 K without decomposition.*

The apparatus used for the distillation under reduced pressure is shown in Fig. 14. The liquid to be distilled is taken in a special two necked flask called Claisen flask. It is fitted with a long capillary tube in the main neck of the flask. The lower end of the tube is dipping in the liquid and is provided with a screw type stop cock so that the flow of air into the flask may be adjusted as required. The thermometer is placed in the other neck of the flask. The side tube of the second neck is connected to a condenser, the open end of which goes into a receiver. The receiver is further connected to a vacuum pump and a manometer which indicates the pressure. The liquid is heated and it distils over at a reduced pressure.

This technique can be used to separate **glycerol from spent lye in soap industry.**

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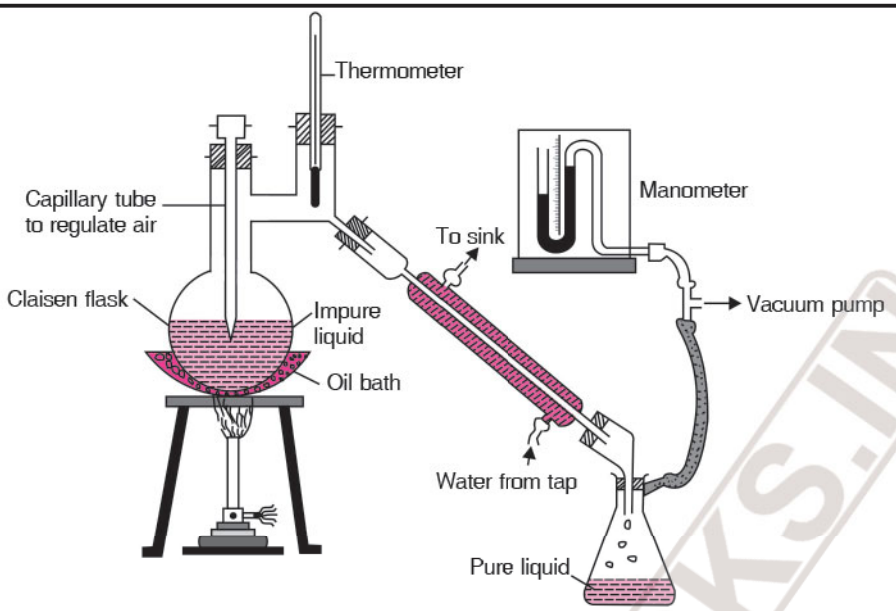

Fig. 14. Distillation under reduced pressure.

7. Steam Distillation

The process of steam distillation is used for the separation and purification of liquid which is appreciably volatile in steam from non-volatile components of a mixture. Thus, the process of steam distillation is used to purify the substances which

(i) are volatile in steam but are not miscible with water.

(ii) possess sufficiently high vapour pressure (about 10–15 mm Hg) at the boiling point temperature of water (100°C).

(iii) contain non-volatile impurities.

In this method, the steam from a steam generator is continuously bubbled through impure organic liquid heated in a flask. Steam heats the liquid but itself gets condensed. After some time, the mixture of the liquid and water starts boiling when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) become equal to atmospheric pressure (p) *i.e.*,

$$p = p_1 + p_2$$

Since p_1 is lower than p, the organic liquid vaporises at lower temperature than its boiling point. At this temperature, the mixture of steam and the liquid gets distilled over and collected in the receiver. The components of mixture are then separated by simple methods. The apparatus is shown in Fig. 15.

Thus, in steam distillation, water and the organic substance vapourise together and the total vapour pressure becomes equal to atmospheric pressure, *i.e.*,

Vapour pressure of organic substance
+ Vapour pressure of water
= Atmospheric pressure

This means that in steam distillation, the organic substance vapourises and gets distilled at lower temperature than its boiling point. The proportion of the organic substance that distils over with steam can be obtained as :

We know from Dalton's law of partial pressures that the partial pressure of different gases in a gaseous mixture are in the ratio of their relative number of moles. Therefore, the ratio of number of moles of organic liquid and water in the distillate will be in the ratio of their partial vapour pressures (in the boiling mixture), *i.e.*

$$\frac{n_1}{n_2} = \frac{p_1}{p_2} \qquad ...(i)$$

where n_1 and n_2 are the number of moles and p_1 and p_2 are the partial pressures of organic liquid and water respectively.

If W_1 and W_2 are the respective masses of the organic liquid and water in the distillate, then

$$n_1 = \frac{W_1}{M} \quad \text{and} \quad n_2 = \frac{W_2}{18}$$

where M is the molecular mass of the organic liquid and 18 stands for the molecular mass of water. Substituting the values of n_1 and n_2 in eqn. (*i*), we get

$$\frac{W_1}{M} \times \frac{18}{W_2} = \frac{p_1}{p_2}$$

or
$$\frac{W_1}{W_2} = \frac{p_1 \times M}{p_2 \times 18} \qquad ...(ii)$$

Equation (*ii*) gives the relative masses of organic liquid and water in the distillate.

The process of steam distillation can be applied for the separation of a mixture of ***o-nitrophenol and p-nitrophenol***. In this process, water vapours carry along with them vapours of *o*-nitrophenol which is more volatile and they get condensed in the receiver ; *p*-nitrophenol with higher boiling point remains in the distillation flask.

This method can also be used for the purification of ***impure sample of aniline***.

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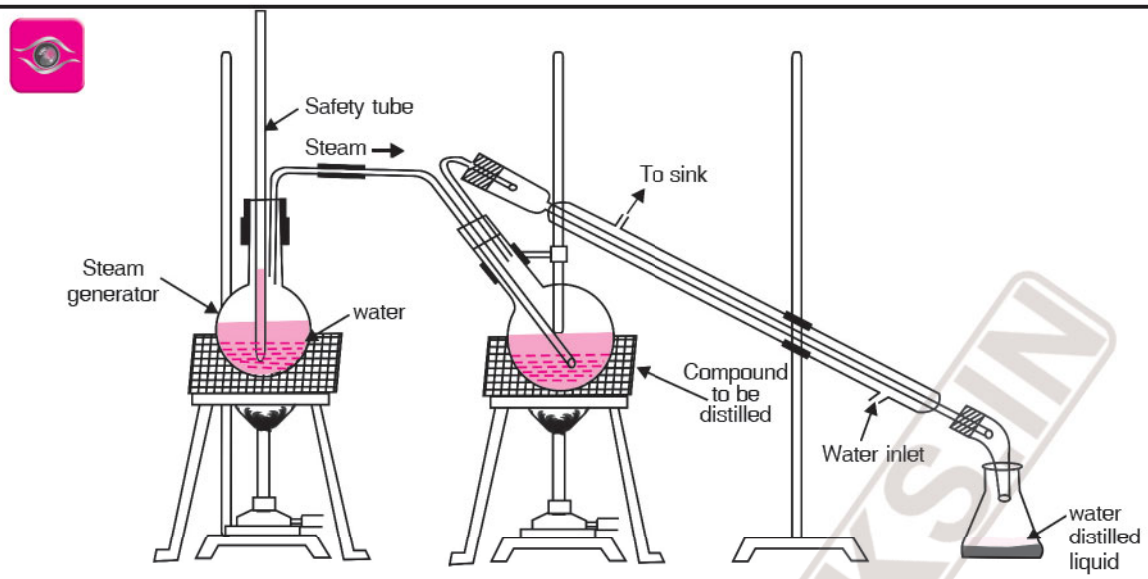

Fig. 15. Steam distillation.

8. Differential Extraction

This method is used to separate a given organic compound present in aqueous solution by shaking with a suitable organic solvent in which the compound is more soluble than water. The basic requirement of the organic solvent is that it should be immiscible with water so that organic and water layers can be easily separated.

For this process, the aqueous solution is mixed with a small quantity of organic solvent in a separating funnel (Fig. 16). The separating funnel is stoppered and its contents are shaken for some time and then the funnel is allowed to stand for some time. The organic liquid and water form separate layers. The two layers are collected by opening the stop cock. The aqueous layer is again transferred to the separating funnel and the process is repeated with more organic solvent. The evaporation of solvent from solvent layer gives the substance. *It may be noted that to have maximum extraction, the process may be repeated a number of times. Greater the number of extractions applied, more will be the amount of substance extracted.* For example, benzoic acid from water may be extracted from its aqueous solution by using benzene. Then benzoic acid may be finally recovered from its solution by distilling off the organic solvent.

This process can also be used to separate two organic liquids such as aniline and water.

It may be noted that when the organic substance is less soluble in the organic solvent, a very large quantity of the solvent would be required to extract even a very small amount of the compound. In such cases, a technique of **continuous extraction** is used. In this method, the same solvent is repeatedly used for the extraction of the compound. The solid mixture containing the compound is taken in a porous tube A fitted with a thick filter paper. The solvent is taken in flask B. When the flask B is heated, the vapours of the solvent rise up and condense in the condenser. The condense liquid falls in tube A and extracts the

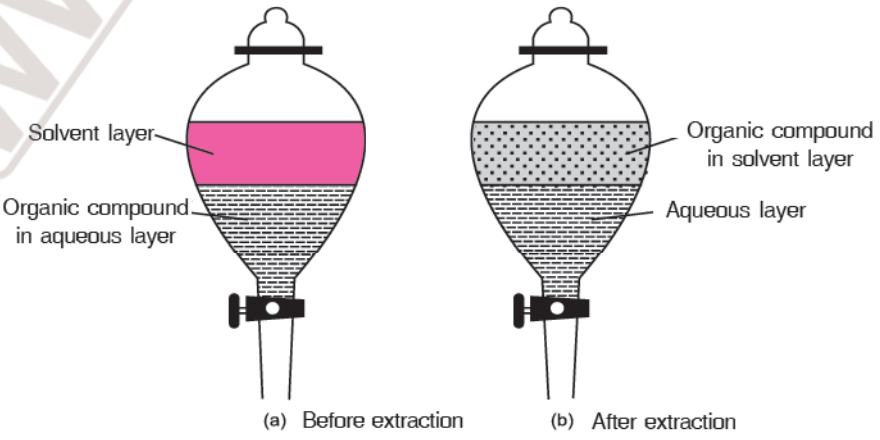

Fig. 16. Differential extraction with separating funnel.

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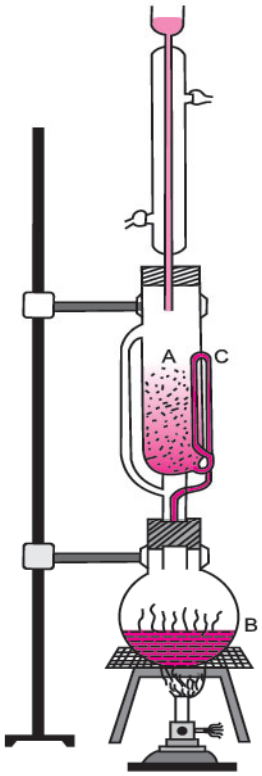

Fig. 17. Continuous differential extraction of a less soluble compound in a solvent.

compound. When the level of the liquid in tube A reaches up to the top in tube C, it gets siphoned and is collected in the flask which is being heated continuously. The solvent is distilled and its vapours again rise, get condensed and extract compound in tube A. Thus, the process of extraction continues.

9. Chromatography

This is a modern method used for the separation of mixtures into its components, purification of compounds and also to test the purity of compounds. The name chromatography is based on the Greek word *chroma* meaning colour and *graphy* for writing because the method was first used for the separation of coloured substances found in plants. This method was described by Tswett in 1903.

Principle of Chromatography

The technique of chromatography is based on ***the difference in the rates at which the components of a mixture move through a porous medium (called stationary phase) under the influence of some solvent or gas (called moving phase).***

Thus, this technique consists of two phases—one of these is a stationary phase of large surface area while the second is a moving phase which is allowed to move slowly over the stationary phase. The stationary phase is either a solid or a liquid while the moving phase may be a liquid or a gas.

The selective removal of the components may be due to adsorption or partitioning (distribution) processes. Based on the principle involved, chromatography is classified into two categories :

A. Adsorption chromatography

B. Partition chromatography.

A. Adsorption Chromatography

It is based on the fact that ***different compounds are adsorbed* on an adsorbent to different degrees.*** When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase because of the different adsorption tendencies. In this case, the stationary phase can be held on a filter paper (paper chromatography), a cylindrical column of solid (column chromatography) or a thin layer of the solid spread on an inert surface (thin layer chromatography).

The following are two main types of chromatographic techniques based on the principle of differential absorption :

(i) Column chromatography

(ii) Thin layer chromatography

1. Column Chromatography

In this method, a suitable adsorbent like *alumina* (Al_2O_3), *silica* (SiO_2), *magnesium oxide* or Fuller's earth is packed as a column in a burette like long tube fitted with stop cock near its bottom. A plug of cotton or glass wool is placed at the bottom of the column to support the adsorbent. This acts as a *stationary phase.*

The mixture to be separated is dissolved in a suitable solvent and the solution is poured on the top of the column of the adsorbent. Because different

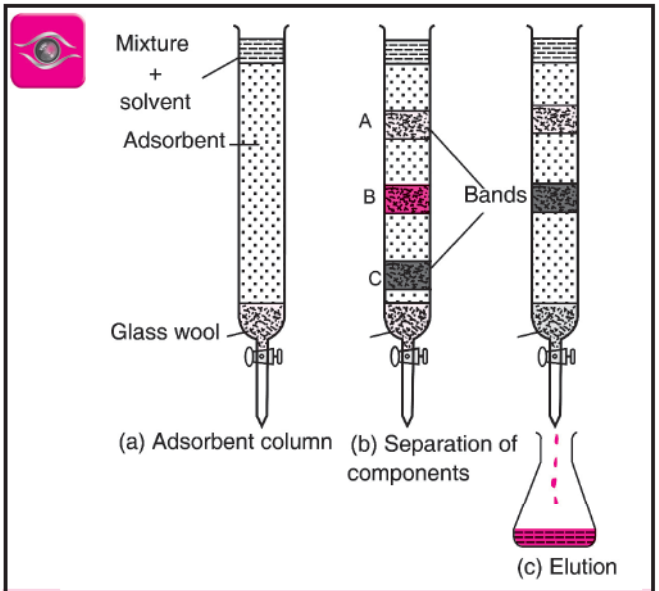

Fig. 18. Column chromatography.

*Adsorption is a phenomenon of higher concentration of molecular species (liquids or gases) on the surface of a solid than in the bulk. The solid substance on the surface of which adsorption occurs is known as **adsorbent** (similar to solvent in case of solution). The substance that gets adsorbed on the solid surface is called **adsorbate** (similar to solute in case of solution).

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components of the mixture are adsorbed to different extents, they get adsorbed to different parts of the column. The component which is adsorbed strongly gets adsorbed at the top. The other components with decreasing orders of their adsorbabilities are held up at different zones down the column in the form of bands. Consider, for example, a mixture of three components A, B and C. Let their tendencies to get adsorbed on a solid surface area in the order A > B > C when these are dissolved in a solvent and passed through the column. The component A, which is most strongly adsorbed by the adsorbent will be held by the solid to a greater extent than the others. It will be adsorbed at the top. As this solution goes down, the concentration of A becomes less and more of B will be adsorbed (adsorbing power of B is more than that of C). After this C will be adsorbed. Thus, a separation of the mixture takes place.

After the separation, the substances are extracted from the adsorbent with suitable solvent. *This process of recovery or extraction of the adsorbed components from the adsorbent with the help of a suitable solvent is called* **elution**. The commonly employed eluents are *petroleum ether, carbon tetrachloride, benzene, alcohol, acetone,* etc. The eluent acts as a *mobile phase.* The eluent dissolves out different components selectively. The weakly adsorbed component will be eluted more rapidly than a more strongly adsorbed component. The process of elution is repeated a number of times to result complete separation. Different components of the mixture are collected in the form of different fractions in separate conical flasks. The components from the eluent are separated by simple methods such as distilling off solvent or separating with the help of separating funnel.

Applications of the method. This method has been used

(i) to separate ortho and para nitro-anilines.

(ii) to separate blue and red dyes.

(iii) to separate and purify plant pigments and other natural products.

2. Thin Layer Chromatography (TLC)

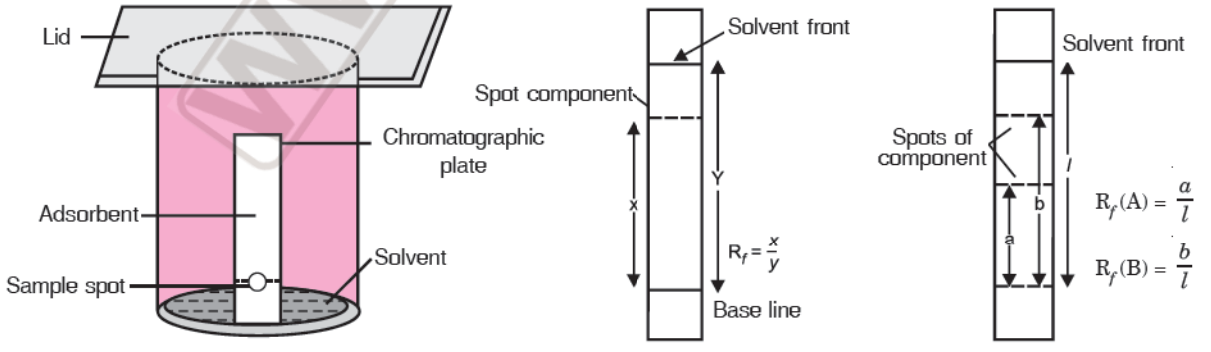
This method involves the separation of the substances of a mixture over a thin layer of an adsorbent coated over a plate. In this method, a thin layer (about 0.2 mm thick) of an adsorbent material (silica gel or alumina or cellulose) is spread over a glass plate of a suitable size as the stationary phase. The plate is called as **thin layer chromatography plate** or **chroma plate.** The solution of the mixture to be separated is applied as a small spot with the help of a fine capillary about 2 cm above one end of the TLC plate. The spot is dried and is placed in a closed jar containing the solvent (eluant) covered with a lid. As the solvent moves up the plate, the components of the mixture move up along the plate to different distances depending upon their degree of adsorption. As a result, separation of the mixture takes place within a few minutes.

The plate is taken out and the position of various spots are visualised by suitable solvents called visualising agents. The movement of the substances relative to the solvent is expressed in terms of its **retention factor,** popularly known as **R_f value.** This gives the relative adsorption of each component of the mixture. It is related to the movement of the solute front relative to the movement of the solvent front as:

$$R_f = \frac{\text{Distance moved by the substance from the base line}}{\text{Distance moved by the solvent from the base line}}$$

The distances are measured from the point of origin (usually the centre of the spot is taken as the origin) as shown in Fig. 19 (*b*). The R_f defines the movement of a substance relative to the solvent and it is constant for a given substance (component) under a given set of conditions. Therefore, it is possible to identify the various components by determining their R_f values. It is also possible to estimate the components quantitatively by measuring the intensity of colours developed by them on reacting with suitable reagents.

In case of mixture of substances, two different spots are obtained as shown in Fig. 19 (*c*). The R_f values of two components may be calculated.



(*a*) Thin layer chromatography apparatus.

(*b*) Developed chromatogram for a compound.

(*c*) Developed chromatogram for a mixture of substances.

Fig. 19

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The spots of coloured compounds are visible on TLC plate due to their original colour. In case of colourless compounds, which are invisible to the eye but which fluoresce can be detected by putting the place under ultra-violet light. There is another method in which the plate is placed in a covered jar containing a few crystals of iodine. Spots of compounds which adsorb iodine will show up as brown spots. Sometimes an appropriate reagent may be sprayed on the plate. For example, amino acids may be detected by spraying the plate with ninhydrin solution.

B. Partition Chromatography

It is based upon the ***differences in the tendencies of substances to distribute or partition between two phases***. In this process, the components of a mixture undergo continuous differential partition between stationary and mobile phases.

Paper chromatography is a type of partition chromatography in which the adsorbent column is a paper strip. It is a special type of paper known as chromatography paper which contains water trapped in it. This acts as a stationary phase.

In this method, a line is drawn by a pencil on the chromatography paper parallel to one edge. Then a drop of the solution of the mixture is applied as a small spot on the line. The spot is dried by blowing hot air over it from a drier.

The chromatographic paper is then suspended in a suitable solvent or a mixture of solvents. Aleternatively, the chromotographic paper is placed in a closed chamber and the edge of the filter paper is dipped into a suitable solvent or a mixture of solvents. These two different methods are shown in Fig. 20 (*a*) and (*b*). The solvent or the solvent mixture to be used depends upon the nature of the components of the mixture. The solvent rises up the paper by capillary action and flows over the spot. The mixture gets separated into its components which also move upwards to different extents, because of their different speeds of movement. The paper selectively retains different components according to their differing partition in two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at differing heights from the position of initial spot on the **chromatogram.** The spots of the separated colourless compounds may be observed either under ultra-violet light or by the use of an appropriate spray reagent as discussed in their layer chromatography.

In addition to above types of chromatography, ion-exchange chromatography, gas chromatography, high performance liquid chromatography (HPLC) are used.

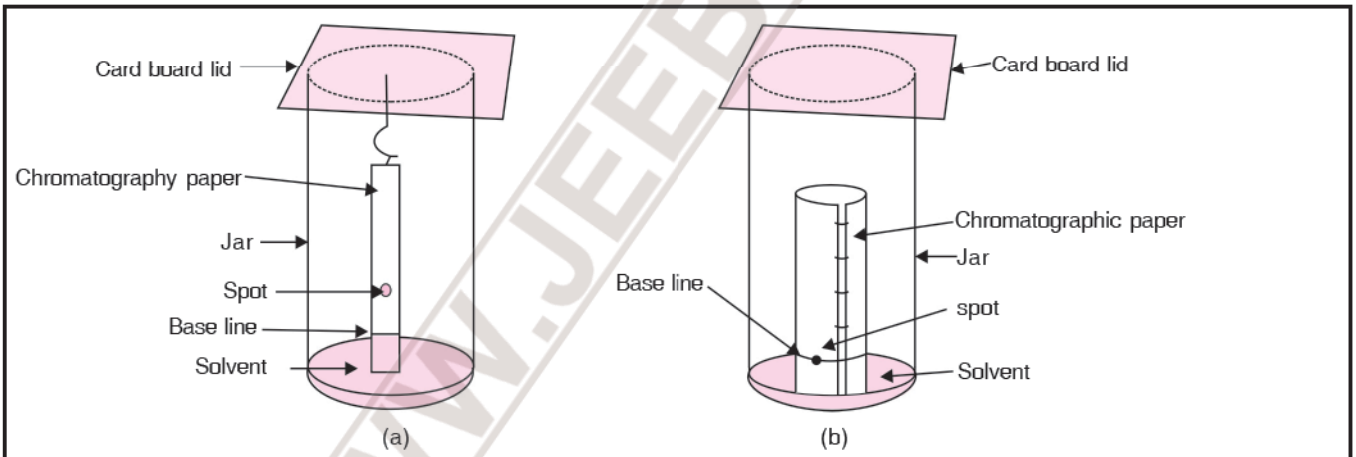

Fig. 20. Paper chromatography.

Practice Problems

13. A liquid has non-volatile impurities. Which method will you use for its purification ?

14. Suggest a method to purify
- (*i*) iodine containing traces of common salt
- (*ii*) kerosene containing water
- (*iii*) benzene containing non-volatile impurities.

15. How will you separate a mixture of *o*-nitrophenol and *p*–nitrophenol ?

16. Who discovered the chromatography technique ?

17. A compound "X" has boiling point of 475 K but it starts decomposing at 400 K. Which type of distillation process is suitable for its purification ?

18. Suggest methods for the separation of following mixtures :
- (*i*) A mixture of liquid A (b.p. = 356 K) and liquid B (b.p. = 365 K)
- (*ii*) A mixture of liquid C (b.p. = 360 K) and liquid D (b.p. = 395 K)
- (*iii*) A liquid 'E' (b.p. = 563 K) having decomposition temperature 450 K.

19. How will you purify an impure sample of (*i*) camphor (*ii*) aniline ?

20. Give two examples of adsorbents used in chromatography.

21. The R_f values of A and B in a mixture determined by TLC in a solvent mixture are 0.65 and 0.42 respectively. If the mixture is separated by column

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chromatography using the same solvent mixture as a mobile phase, which of the two components A or B will elute first ?

22. Name the method of separating naphthalene from kerosene present in a mixture.

23. A mixture contains 71% of calcium sulphate and 29% of camphor. Name a suitable technique of separation of the components of the mixture.

Answers to Practice Problems

13. Distillation

14. (*i*) Sublimation (*ii*) solvent extraction method (*iii*) distillation.

15. By steam distillation.

16. Tswett.

17. Distillation under reduced pressure.

18. (*i*) Fractional distillation (*ii*) Simple distillation (*iii*) Distillation under reduced pressure.

19. (*i*) Sublimation (*ii*) Steam distillation

20. Alumina (Al_2O_3), silica gel.

21. A

22. Fractional extraction.

23. Sublimation method.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The qualitative analysis of an organic compound involves the detection of all the elements present in it. *Carbon* and *hydrogen* are generally present in all the organic compounds. The other elements which may be present in organic compounds are oxygen, nitrogen, sulphur, halogens, phosphorus. These can be detected by the following tests :

1. Detection of Carbon and Hydrogen

A small amount of the dry and powdered substance is mixed with about double the amount of pure and dry copper oxide. The mixture is heated in a well dried hard glass tube provided with a delivery tube having a bulb in the centre (Fig. 21). The other end of the delivery tube is dipped in a tube containing lime water. The bulb in the delivery tube is packed with glass wool containing anhydrous copper sulphate (white). When the mixture is heated, the carbon present in the compound is oxidised to carbon dioxide which turns lime water milky. The hydrogen present in the organic compound is oxidised to water which turns anhydrous copper sulphate in the bulb to blue.

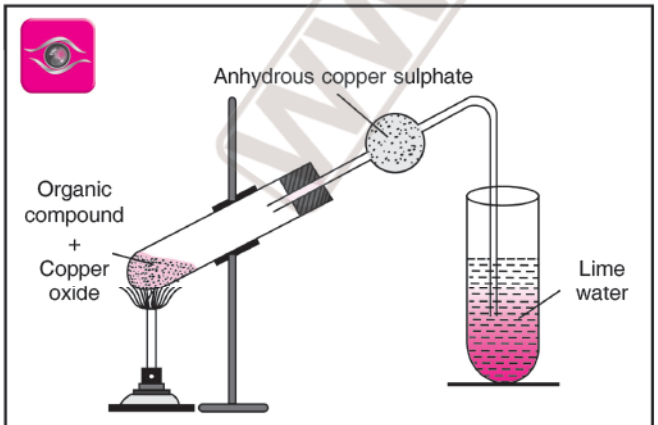

Fig. 21. Detection of carbon and hydrogen in an organic compound.

$$\underset{\text{From organic compound}}{C} + 2CuO \xrightarrow{\text{Heat}} \underset{\text{(dry)}}{CO_2} + 2Cu$$

$$CO_2 + \underset{\text{Lime water}}{Ca(OH)_2} \longrightarrow \underset{\text{Milky solution}}{CaCO_3} + H_2O$$

$$\underset{\text{From organic compound}}{2H} + CuO \xrightarrow{\text{Heat}} H_2O + Cu$$

$$\underset{\substack{\text{Anhydrous copper sulphate} \\ \text{(white)}}}{CuSO_4} + 5H_2O \longrightarrow \underset{\substack{\text{Hydrated copper sulphate} \\ \text{(blue)}}}{CuSO_4 . 5H_2O}$$

This method is known as **copper oxide test.** If the organic compound is volatile liquid or a gas, then the vapour of the liquid or gas itself is passed through heated copper oxide and the liberated gases are tested for CO_2 (with lime water) and water vapours (with anhydrous $CuSO_4$).

2. Detection of Nitrogen

Nitrogen in an organic compound is detected by the following tests :

(*a*) Soda lime test. A pinch of an organic compound is heated strongly with soda lime (NaOH + CaO) in a test tube. *If ammonia gas evolves, it indicates nitrogen.*

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NaOH \xrightarrow{CaO} CH_3COONa + NH_3$$

Limitation. This method has a limitation. A large number of organic compounds such as *nitro* (*–NO_2*) and *diazo* (–N=N–) compounds do not liberate ammonia on heating with soda lime.

(*b*) Lassaigne's test. This is the most reliable test for the detection of nitrogen. It is carried out as follows :

A small piece of a dry sodium metal is heated gently in a fusion tube till it melts to a *shining globule*. Then, a small amount of organic substance is added and the tube is heated strongly till it becomes red hot. The red hot tube is plunged into distilled water contained in a china dish and boiled for some time. It is then cooled and filtered. The filtered liquid is known as **sodium extract** or **Lassaigne's extract.**

The Lassaigne's extract is usually alkaline. If not, it may be made alkaline by adding a few drops of a dilute solution of sodium hydroxide. To a part of sodium extract a small amount of a freshly prepared ferrous sulphate solution is added and the contents are

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warmed. A few drops of ferric chloride solution are then added to the contents and the resulting solution is acidified with dilute hydrochloric acid. The appearance of a **bluish green** or a **prussian blue** colouration confirms the presence of nitrogen in the organic compound.

The following chemical reactions occur during the test :

$$Na + \underbrace{C+N}_{\text{From organic compound}} \longrightarrow NaCN$$

$$FeSO_4 + 2NaCN \longrightarrow Fe(CN)_2 + Na_2SO_4$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{Sodium hexacyanoferrate (II)}}{Na_4[Fe(CN)_6]}$$

Sodium ferrocyanide

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Iron (III) hexacyanoferrate (II)}}{Fe_4[Fe(CN)_6]_3} + 12\,NaCl$$

Ferric ferrocyanide (Prussian blue)

or $Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

Note. If the organic substance contains nitrogen and sulphur together, sodium thiocynate may be formed in the sodium extract which gives **blood red colouration** with ferric chloride due to the formation of ferric thiocyanate.

$$Na + \underbrace{C+N+S}_{\text{From organic compound}} \longrightarrow \underset{\text{Sodium thiocyanate}}{NaCNS}$$

$$3NaCNS + FeCl_3 \longrightarrow \underset{\text{Ferric thiocyanate (Blood red)}}{Fe(CNS)_3} + 3NaCl$$

or $Fe^{3+} + 3\,CNS^- \longrightarrow \underset{\text{Ferric thiocyanate (Blood red)}}{[Fe(CNS)_3]}$

However, it may be noted that the absence of blood red colouration in this test does not necessarily mean that sulphur is absent. This is because if sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests :

$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

3. Detection of Sulphur

Sulphur in an organic compound can also be detected by Lassaigne's test. Sodium extract or Lassaigne solution is prepared as described earlier. The sulphur in the compound reacts with sodium metal to form sodium sulphide.

$$2Na + \underset{\text{From organic compound}}{S} \longrightarrow Na_2S$$

The Lassaigne's extract is divided into two parts and following tests are performed :

***(i)* Sodium nitroprusside test.** To one portion of the extract, a few drops of sodium nitroprusside are added. The appearance of *violet colouration* indicates sulphur.

$$\underset{\text{Sod. nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Violet colouration}}{Na_4[Fe(CN)_5NO.S]}$$

or $S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow \underset{\text{Violet}}{[Fe(CN)_5\,NOS]^{4-}}$

***(ii)* Lead acetate test.** The other part of the Lassaigne's extract is acidified with acetic acid and then lead acetate solution is added. Formation of black precipitate confirms the presence of sulphur.

$$\underset{\text{Lead acetate}}{Na_2S + Pb(CH_3COO)_2} \longrightarrow \underset{\text{Black}}{PbS} + 2CH_3COONa$$

4. Detection of Halogens

Halogens in an organic compound are detected by the following tests :

1. Beilstein's test. A clean copper wire is heated in the non-luminous flame till it does not impart blue colour to flame. The hot end of copper wire is now touched with the organic substance and is again introduced into flame. The reappearance of green or blue colour indicates the presence of halogens in the organic compound.

Limitation. *(i)* This test is given by substances such as *urea, thiourea,* etc. which do not contain halogens.

(ii) It does not tell as to which halogen is present.

2. Lassaigne's test. Sodium extract is prepared as already described. During fusion, sodium will combine with the halogen (from the organic compound) to form sodium halide.

$$Na + X \xrightarrow{\text{Fusion}} NaX\ (X = Cl, Br, I)$$

The extract is acidified with concentrated nitric acid and boiled to expel the gases. It is then cooled and a small amount of silver nitrate is added. The formation of white or yellow precipitate confirms halogens.

(i) A white precipitate soluble in ammonium hydroxide solution indicates the presence of **chlorine** in the organic compound.

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl} + NaNO_3$$

(ii) A dull yellow precipitate partially soluble in ammonium hydroxide solution indicates the presence of **bromine** in the organic compound.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{Dull yellow ppt.}}{AgBr} + NaNO_3$$

(iii) A bright yellow precipitate, completely insoluble in ammonium hydroxide solution, indicates the presence of **iodine** in the organic compound.

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$$NaI + AgNO_3 \longrightarrow \underset{\text{Bright yellow ppt.}}{AgI} + NaNO_3$$

Function of nitric acid. In case, nitrogen and sulphur are present along with the halogens in the organic compound, the Lassaigne's extract contains sodium sulphide (Na_2S) and sodium cyanide (NaCN) along with sodium halide. These will form precipitates with silver nitrate solution. Therefore, nitric acid is added to decompose sodium cyanide and sodium sulphide.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN$$

$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S$$

Special test for bromine and iodine. Boil a portion of the Lassaigne's extract with nitric acid. Add a few drops of carbon disulphide and then add chlorine water slowly with constant shaking.

An **orange colouration** in carbon disulphide layer confirms the presence of **bromine** whereas a **violet colouration** in the layer confirms the presence of **iodine**.

$$2NaBr + Cl_2 \longrightarrow \underset{\text{(turns } CS_2 \text{ layer orange)}}{2NaCl + Br_2}$$

$$2NaI + Cl_2 \longrightarrow \underset{\text{(turns } CS_2 \text{ layer violet)}}{2NaCl + I_2}$$

5. Detection of Phosphorus

To detect the presence of phosphorus, the given organic compound is fused with sodium peroxide (oxidising agent).

$$\underset{\text{From organic compound}}{2P} + 5Na_2O_2 \xrightarrow{\text{Heat}} 2Na_3PO_4 + 2Na_2O$$

The fused mass is extracted with water. The filtrate obtained is boiled with a few drops of conc. HNO_3. Then the solution is treated with ammonium molybdate. A yellow coloured precipitate (due to ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$ confirms phosphorus).

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12\,(NH_4)_2\,MoO_4 + 21HNO_3 \longrightarrow$$

$$\underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3\,PO_4 \cdot 12\,MoO_3} + 21\,NH_4NO_3 + 12\,H_2O$$

6. Detection of Oxygen

There is no direct method to detect oxygen in an organic compound. However, it can be tested by testing the presence of oxygen containing functional groups (such as —OH, —CHO, —COOH, $—NO_2$, etc). The presence of these functional groups confirms the presence of oxygen in the organic compound.

Practice Problems

- **24.** Name a compound which does not contain halogen but gives positive Beilstein's test.
- **25.** What will happen during Lassaigne's test for nitrogen if the compound also contains sulphur ?
- **26.** What precipitate will occur when silver nitrate is added to chloroform ?
- **27.** Why is the organic compound fused with sodium metal before testing for N or halogen ?

Answers to Practice Problems

- **24.** Urea
- **25.** Blood red colouration due to $Fe(CNS)_3$ will be produced.
- **26.** No ppt.
- **27.** No ppt.

QUANTITATIVE ANALYSIS

Quantitative analysis involves the determination of the percentages of the various elements present in a given compound. The common methods are discussed below :

1. Estimation of Carbon and Hydrogen

Carbon and hydrogen in the organic compound are estimated by **Liebig's method.**

Principle. A known mass of the given dry organic compound is heated strongly with dry cupric oxide in an atmosphere of air or oxygen free from CO_2. The carbon and hydrogen of the organic compound are oxidised to CO_2 and water vapour as :

$$\underset{\text{(from compound)}}{C} + 2CuO \xrightarrow{\text{Heat}} CO_2 + 2Cu$$

$$\underset{\text{(from compound)}}{2H} + CuO \xrightarrow{\text{Heat}} H_2O + Cu$$

In general,

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow x\,CO_2 + \frac{y}{2}\,H_2O$$

Carbon dioxide produced is collected in *potash bulbs* (containing KOH solution) while water vapour are absorbed in *anhydrous calcium chloride* tubes. From the amounts of carbon dioxide and water vapour produced, the percentage of carbon and hydrogen can be calculated.

Procedure. The apparatus for estimation of C and H is shown in Fig. 22. The substance is heated with CuO. The carbon dioxide thus produced is absorbed in a U-tube containing a strong solution of KOH while water produced is absorbed in a U-tube containing anhydrous calcium chloride. These tubes are weighed before and after the combustion. The increase in masses after the experiment gives the amount of water and CO_2 produced.

Let the mass of organic compound taken = w g

Mass of water formed = m_1 g
(increase in $CaCl_2$ U-tube)

Mass of carbon dioxide formed = m_2 g
(increase in potash tubes)

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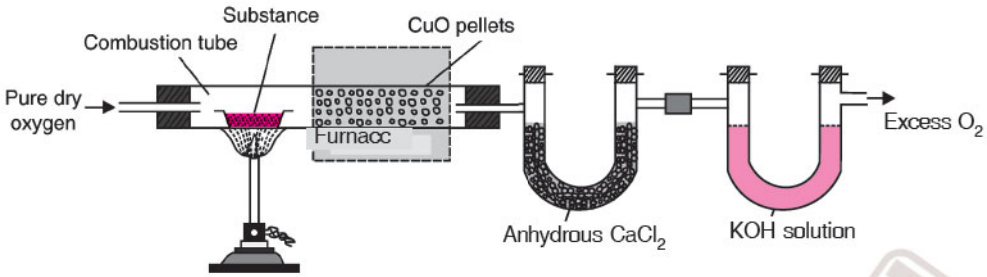

Fig. 22. Apparatus for the estimation of C and H.

Percentage of Carbon

We know that 1 mole of carbon dioxide (44 g) contains 1 gram atom of carbon (12 g)

$$CO_2 \equiv C$$

$$44 \text{ g of } CO_2 \text{ contain C} = 12 \text{ g}$$

$$\therefore \quad m_2 \text{ g of } CO_2 \text{ contain C} = \frac{12}{44} \times m_2 \text{ g}$$

$$\text{Hence,} \quad \text{Percentage of carbon} = \frac{12 \times m_2}{44 \times w} \times 100$$

$$\textbf{Percentage of C} = \frac{12}{44} \times \frac{\textbf{Mass of } CO_2 \textbf{ formed}}{\textbf{Mass of compound taken}} \times 100$$

Percentage of Hydrogen

We know that one mole of water (18 g) contains 2 gram atom of hydrogen (2 g)

$$H_2O \equiv 2H$$

$$18 \text{ g of } H_2O \text{ contain H} = 2\text{g}$$

$$\therefore \quad m_1 \text{ g of } H_2O \text{ contains H} = \frac{2}{18} \times m_1 \text{ g}$$

$$\text{Percentage of hydrogen} = \frac{2m_1}{18 \times w} \times 100.$$

$$\textbf{Percentage of H} = \frac{2}{18} \times \frac{\textbf{Mass of } H_2O \textbf{ formed}}{\textbf{Mass of compound taken}} \times 100$$

SOLVED EXAMPLES

Example 31. *0.2475 g of an organic compound gave on combustion 0.4950 g of carbon dioxide and 0.2025 g of water. Calculate the percentage of carbon and hydrogen in it.*

Solution:

Wt. of organic compound = 0.2475 g

Wt. of CO_2 produced = 0.4950 g

Wt. of H_2O produced = 0.2025 g

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{\text{Wt. of } CO_2}{\text{Wt. of compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{\text{Wt. of } H_2O}{\text{Wt. of compound}} \times 100$$

$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = \mathbf{9.09}$$

Example 32. *An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.* ***N.C.E.R.T.***

Solution :

Percentage of carbon = 69%

$$\text{Amount of carbon in 0.20 g of compound} = 0.2 \times \frac{69}{100}$$

$$= 0.138 \text{ g}$$

Percentage of hydrogen = 4.8%

$$\text{Amount of hydrogen in 0.20 g of compound} = \frac{0.2 \times 4.8}{100}$$

$$= 0.0096 \text{ g}$$

Now $C \equiv CO_2$

12 g of carbon on combustion give CO_2 = 44 g

$$0.138 \text{ g of carbon on combustion give } CO_2 = \frac{44}{12} \times 0.138$$

$$= \mathbf{0.506 \text{ g}}$$

$2H \equiv H_2O$

2 g of hydrogen on combustion give water = 18 g

$$0.0096 \text{ g of hydrogen on combustion give water} = \frac{18}{2} \times 0.0096$$

$$= \mathbf{0.0864 \text{ g}}$$

Example 33. *On complete combustion, 0.246 g of an organic compound gave 0.198 g of carbon dioxide and 0.1014 g of water Calculate the percentage composition of carbon and hydrogen in the compound.*

N.C.E.R.T.

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Solution :

Wt. of organic compound = 0.246 g

Wt. of CO_2 produced = 0.198 g

Wt. of H_2O produced = 0.1014 g

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{0.198 \times 100}{0.246}$$

$$= 20.95\%$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{0.1014 \times 100}{0.246}$$

$$= 4.58\%$$

2. Estimation of Nitrogen

There are two methods for the estimation of nitrogen :

(*i*) *Duma's method* (*ii*) *Kjeldahl's method*

(*i*) **Duma's method.** This method is based upon the following principle :

Principle of the method. A known mass of an organic compound is heated with dry cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen are oxidised to carbon dioxide and water respectively while nitrogen is set free. If any oxide of nitrogen is produced during this process, it is reduced to nitrogen by passing over a heated copper gauze. The gaseous mixture is collected over an aqueous solution of KOH, when all the gases except nitrogen are absorbed. The volume of nitrogen produced is measured at room temperature and atmospheric pressure. From the volume of N_2 produced, percentage of nitrogen in the sample can be calculated. The following reactions take place during this process :

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

$$2H + CuO \longrightarrow H_2O + Cu$$

$$2N + CuO \longrightarrow N_2 + \text{oxides of nitrogen}$$

$$\text{Oxides of nitrogen} + Cu \longrightarrow CuO + N_2$$

In general,

$$C_xH_yN_z + (2x + \frac{y}{2})\,CuO \longrightarrow x\,CO_2 + \frac{y}{2}\,H_2O + \frac{z}{2}\,N_2 + (2x + \frac{y}{2})\,Cu$$

Procedure. The apparatus for the estimation of nitrogen by Duma's method is shown in Fig. 23. A known mass of the organic compound is heated with a dry cupric oxide in a combustion tube in the atmosphere of CO_2. The CO_2 is produced by heating sodium bicarbonate and the gas is bubbled through conc. H_2SO_4 to free it from moisture. A roll of oxidised copper gauze is placed in the combustion tube which prevents the backward diffusion of the gases evolved in combustion. The organic compound is oxidised by a layer of coarse copper oxide that fills about two-third of the combustion tube. On heating, carbon and hydrogen present in the organic compound are oxidised to carbon dioxide and water vapours respectively while nitrogen is set free.

During heating a small amount of nitrogen might be oxidised to its oxides but they are reduced back to nitrogen by reduced copper placed at the end of combustion tube.

$$\text{Oxides of nitrogen} + Cu \longrightarrow CuO + N_2$$

The gaseous vapours are then passed into Schiff's nitrometer tube which contains about 40% KOH solution. It has a mercury seal at the bottom to check the backward flow of the liquid. The volume of nitrogen at the atmospheric pressure is recorded with the help of reservoir. Both CO_2 and H_2O vapours are absorbed by KOH solution while nitrogen is collected over it. Its volume is recorded after careful levelling (by making the level of KOH solution in the nitrometer tube and reservoir the same). The room temperature is recorded and the aqueous tension of water vapours at this temperature is noted from the tables.

Let the mass of organic compound = w g

The volume of nitrogen collected = V mL

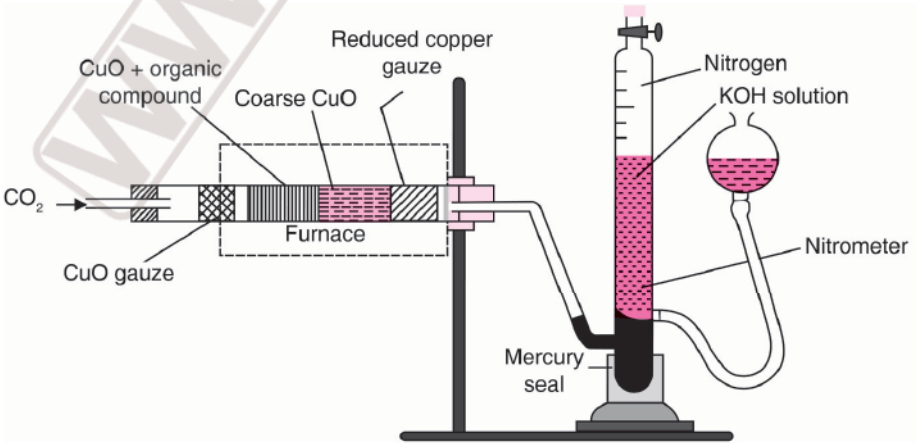

Fig. 23. Estimation of nitrogen by Duma's method.

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Atmospheric pressure (from barometer)= $p$mm of Hg

Room temperature = T_1K

If temperature is in °C, then $T_1K = t°C + 273$

Aqueous tension at $T_1K = a$ mm of Hg

Pressure of dry nitrogen = $(p - a)$ mm of Hg

Let us first convert the volume of nitrogen to volume at S.T.P.

Experimental conditions	*S.T.P. conditions*
$p_1 = (p - a)$mm Hg	$p_2 = 760$ mm Hg
$T_1 = T_1K$	$T_2 = 273$ K
$V_1 = V$ mL	$V_2 = ?$

Applying gas equation, $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$

$$\therefore V_2 = \frac{p_1 V_1 T_2}{p_2 T_1} = \frac{(p-a) \times V \times 273}{760\ T_1} = x \text{ mL (say)}$$

Now, 22,400 mL of N_2 at S.T.P. will weigh = 28 g

x mL of N_2 at S.T.P. will weigh = $\frac{28}{22400} \times x$ g

$\therefore$ Percentage of nitrogen

$$= \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100$$

$$= \frac{28\ x \times 100}{22400 \times w}$$

Percentage of N =

$$\frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at S.T.P}}{\text{Mass of compound taken}} \times 100$$

(*ii*) **Kjeldahl's method.** This method is *simpler and more convenient* than Duma's method. This method is largely used for the estimation of nitrogen in food stuffs, drugs, fertilizers and many other organic compounds.

However, this method cannot be used for

(i) organic compounds containing nitrogen in the ring such as *pyridine, quinoline,* etc.

(ii) organic compounds containing *nitro* (—NO_2) and *diazo* (— N = N —) groups.

Principle. A known mass of the organic compound is heated with conc.H_2SO_4 so that nitrogen is quantitatively converted into ammonium sulphate. The resulting solution is then heated with excess of sodium hydroxide. The ammonia gas evolved is passed into a known but excess volume of standard acid (HCl or H_2SO_4).

$$\underset{\text{(From organic compound)}}{C, H, S} \xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4} CO_2 + H_2O + SO_2$$

$$\underset{\text{(From organic compound)}}{N} \xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4} \underset{\text{Ammonium sulphate}}{(NH_4)_2\ SO_4}$$

$$(NH_4)_2\ SO_4 + 2NaOH \xrightarrow{\text{Heat}} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

or $$NH_3 + HCl \longrightarrow NH_4Cl$$

The acid left unused is estimated by titrating the solution with standard alkali.

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

From the amount of acid left unused, the amount of acid used for neutralisation of ammonia can be calculated. From this percentage of nitrogen can be calculated.

Procedure. The apparatus is shown in Fig. 24. The compound (about 0.5 g) is heated with conc. H_2SO_4 in a Kjeldahl's flask, which is a round bottomed flask having a long neck provided with a loose stopper. A small amount of potassium sulphate and a little of mercury (or copper sulphate) are added. The former raises the boiling point of sulphuric acid while the latter acts as catalyst. The heating is done for 2-3 hours when carbon and hydrogen present in the compound are oxidised to carbon dioxide and water vapours respectively while nitrogen is converted into ammonium sulphate.

Carbon dioxide and water vapours escape through the loose stopper whereas ammonium sulphate remains in the flask. The contents of the flask are cooled and transferred to a round bottomed flask. These are diluted with water and a few drops of indicator methyl orange are added. The indicator will give pink colour showing acidic nature of the solution.

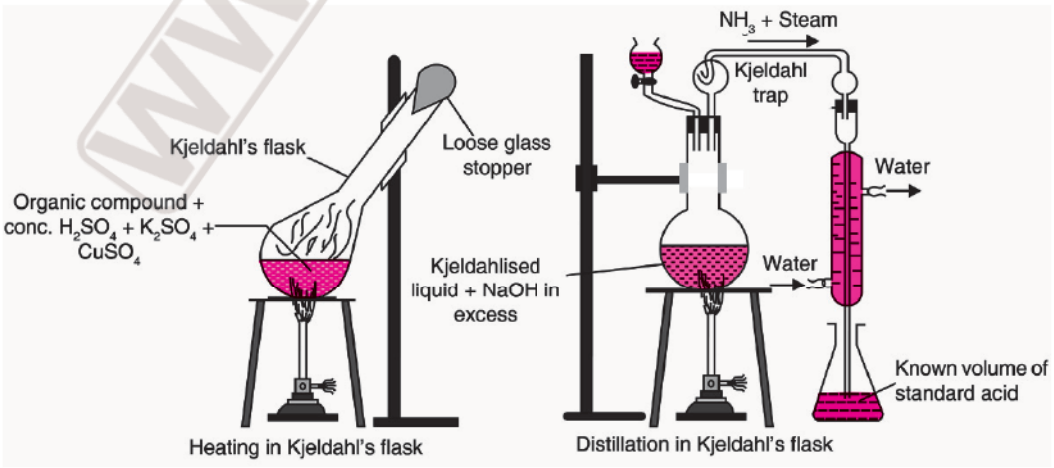

Fig. 24. Estimation of nitrogen by Kjeldahl's method.

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The flask is fitted with a dropping funnel. About 40% solution of NaOH is added with the help of dropping funnel and the flask is heated. During heating, ammonia is liberated which passes through the trap which retains water. The ammonia vapours are condensed and the liquid ammonia formed is absorbed in a known excess of standard solution of sulphuric acid. The unreacted (or excess) acid left after absorption of ammonia is estimated by titration with standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.

Calculations

Let the mass of organic compound = w g

Volume of standard H_2SO_4 of molarity M = V mL

Now, excess acid left after absorption of NH_3 is titrated with NaOH of molarity, M.

Let volume of NaOH of molarity M used for titration of excess of H_2SO_4 = V_1 mL

Now,

V_1 mL of NaOH of molarity M $\equiv \frac{V_1}{2}$ mL of H_2SO_4 of molarity M

$\therefore$ Volume of H_2SO_4 of molarity M left unreacted

$$= \frac{V_1}{2} \text{ mL}$$

Volume of H_2SO_4 of molarity M used for neutralisation of $NH_3 = \left(V - \frac{V_1}{2}\right)$ mL

Now,

$\left(V - \frac{V_1}{2}\right)$ mL of H_2SO_4 of molarity M $\equiv 2\left(V - \frac{V_1}{2}\right)$ mL of NH_3 solution of molarity M

$\therefore$ Volume of NH_3 evolved $= 2\left(V - \frac{V_1}{2}\right)$ mL of molarity M

Now, 1000 mL of 1 M NH_3 solution contain 17 g NH_3 or 14 g nitrogen

$2\left(V - \frac{V_1}{2}\right)$ mL of NH_3 of molarity M contains

$$\text{nitrogen} = \frac{14 \times M \times 2\left(V - \frac{V_1}{2}\right) \text{ g}}{1000}$$

$$\text{Percentage of N} = \frac{14 \times M \times 2\left(V - \frac{V_1}{2}\right) \text{ g}}{1000} \times \frac{100}{w}$$

or

$$= \frac{1.4 \times M \times 2\left(V - \frac{V_1}{2}\right)}{w}$$

Percentage of N =

$$\frac{1.4 \times \text{Molarity of acid} \times \text{Basicity of acid} \times \text{Volume of acid used}}{\text{Mass of compound taken}}$$

(*e.g.* for H_2SO_4, basicity = 2)

For monobasic acids (basicity = 1)

Percentage of N =

$$\frac{1.4 \times \text{Molarity of acid} \times \text{Volume of acid used}}{\text{Mass of compound taken}}$$

or

$$= \frac{1.4 \times \text{Normality of acid} \times \text{Volume of acid used}}{\text{Mass of compound taken}}$$

($\because$ for monobasic acids, molarity = normality)

SOLVED EXAMPLES

Example 34.

In a Duma's nitrogen estimation, 0.3 g of an organic compound gave 50 mL of nitrogen collected at 300 K and 715 mm pressure. Calculate the percentage of nitrogen in the compound (vapour pressure of water at 300 K is 15 mm).

Solution : Vapour pressure of gas = 715 – 15 = 700 mm

To calculate the volume of N_2 at S.T.P.

V_1 = 50 mL	V_2 = ?
p_1 = 700 mm	p_2 = 760 mm
T_1 = 300 K	T_2 = 273 K

Applying $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

or $V_2 = \frac{p_1V_1T_2}{p_2T_1}$

$\therefore$ $V_2 = \frac{700 \times 50 \times 273}{760 \times 300}$

= 41.9 mL

22400 mL of nitrogen at S.T.P. weigh = 28 g

41.9 mL of nitrogen at S.T.P. weigh $= \frac{28 \times 41.9}{22400}$

= 0.0524 g

Percentage of nitrogen $= \frac{0.0524}{0.3} \times 100 =$ **17.46%.**

Example 35.

During nitrogen estimation of an organic compound by Kjeldahl's method, the ammonia evolved by 0.5 g of the compound neutralised 10 mL of 1 M H_2SO_4. Calculate the percentage of nitrogen in the compound.

Solution :

1 M of 10 mL H_2SO_4 $\equiv$ 1 M of 20 mL of NH_3

1000 mL of 1 M ammonia contain = 14 g nitrogen

20 mL of 1 M ammonia contain $= \frac{14 \times 20}{1000}$ g nitrogen

$\therefore$ Percentage of nitrogen $= \frac{14 \times 20}{1000 \times 0.5} \times 100$

= **56.0%**

Example 36.

0.257 g of an organic substance was heated with conc. H_2SO_4 and then distilled with excess of

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strong alkali. The ammonia gas evolved was absorbed in 50 mL of M/10 HCl which required 23.2 mL of M/10 NaOH for neutralisation at the end of the process. Determine the percentage of nitrogen in the compound.

Solution : Volume of $\frac{M}{10}$ HCl taken = 50 mL

Volume of $\frac{M}{10}$ NaOH used for neutralisation of unused acid = 23.2 mL

Now,

23.2 mL of $\frac{M}{10}$ NaOH ≡ 23.2 mL of $\frac{M}{10}$ HCl

∴ Volume of $\frac{M}{10}$ HCl unused = 23.2 mL

Volume of $\frac{M}{10}$ HCl required for neutralisation of NH_3 = 50 – 23.2 = 26.8 mL

26.8 mL of $\frac{M}{10}$ HCl ≡ 26.8 mL of M/10 NH_3

1000 mL of 1 M NH_3 solution contains nitrogen = 14 g

26.8 ml of $\frac{M}{10}$ NH_3 solution contains nitrogen

$$= \frac{14 \times 26.8}{10 \times 1000}$$

$$\text{Percentage of nitrogen} = \frac{14 \times 26.8 \times 100}{10 \times 1000 \times 0.257}$$

$$= \mathbf{14.6\%}.$$

Example 37.

0.35 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 mL of M/10 H_2SO_4. The excess acid required 154 mL of M/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

Solution : Vol. of M/10 H_2SO_4 taken = 100 mL

Let us first calculate the volume of excess M/10 H_2SO_4 which was neutralised by 154 mL of M/10 NaOH

154 mL of $\frac{M}{10}$ NaOH ≡ $\frac{154}{2}$ mL of $\frac{M}{10}$ H_2SO_4

∴ Volume of $\frac{M}{10}$ H_2SO_4 left unused = 77 mL

Volume of $\frac{M}{10}$ H_2SO_4 used for neutralisation of NH_3 = 100 – 77 = 23 mL

Now,

23 mL of $\frac{M}{10}$ H_2SO_4 ≡ 2 × 23 mL of $\frac{M}{10}$ NH_3

≡ 46 mL of $\frac{M}{10}$ NH_3

Now 1000 mL of 1 M NH_3 contain nitrogen = 14 g

46 mL of $\frac{M}{10}$ NH_3 contain nitrogen

$$= \frac{14}{1000} \times \frac{46 \times 1}{10}$$

$$\therefore \text{Percentage of nitrogen} = \frac{14 \times 46 \times 100}{1000 \times 10 \times 0.35}$$

$$= \mathbf{18.4\%}$$

Example 38.

A sample of a 0.50 g of an organic compound was heated according to Kjeldahl's method. The ammonia evolved by absorbed in 50 mL of 0.5 M H_2SO_4. The residual acid required 60 mL of 0. 5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

Solution : ***N.C.E.R.T.***

Mass of organic compound taken = 0.50 g

Vol. of 0.5 M H_2SO_4 taken = 50 mL

The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation

60 mL of 0.5 M NaOH solution

$$\equiv \frac{60}{2} \text{ mL of 0.5 M } H_2SO_4 \text{ solution}$$

≡ 30 mL of 0.5 M H_2SO_4 solution

Volume of 0.5 M H_2SO_4 used = 50 – 30 = 20 mL

Now

20 mL of 0.5 M H_2SO_4 ≡ 2 × 20 mL of 0.5 M NH_3 solution

or ≡ 40 mL of 0.5 M NH_3 solution

1000 mL of 1 M NH_3 contain nitrogen = 14 g

40 mL of 0.5 M NH_3 contain nitrogen = $\frac{14 \times 40 \times 0.5}{1000}$

$$\% \text{ of N} = \frac{14 \times 40 \times 0.5}{1000 \times 0.50} \times 100$$

$$= \mathbf{56\%}$$

3. Estimation of Halogens

Halogens are estimated by **Carius method.**

Principle. A known mass of the organic substance is heated with fuming HNO_3 in a Carius tube. The silver halide so obtained is separated, washed, dried and weighed. From the weight of silver halide formed, the percentage of halogen can be calculated.

$$\underset{\text{Halogen}}{X} + AgNO_3 \longrightarrow AgX$$

Carbon, hydrogen or sulphur present in the compound will be oxidised to CO_2, H_2O and H_2SO_4 respectively.

$$C + 2O \xrightarrow{HNO_3} CO_2$$

$$2H + O \xrightarrow{HNO_3} H_2O$$

$$S + H_2O + 3O \xrightarrow{HNO_3} H_2SO_4$$

Procedure. A small amount (about 0.5 g) of silver nitrate and 5 cm^3 of fuming HNO_3 are taken in the Carius tube. A small amount of weighed organic substance taken in a small tube, is also placed carefully into the Carius tube. The tube is placed in an outer iron jacket and is heated in a furnace at 553–563 K

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for 5–6 hours when carbon, hydrogen and sulphur present in the compound are oxidised respectively to carbon dioxide, water vapours and sulphuric acid. The halogen (X) present in the compound is converted to silver halide which is precipitated.

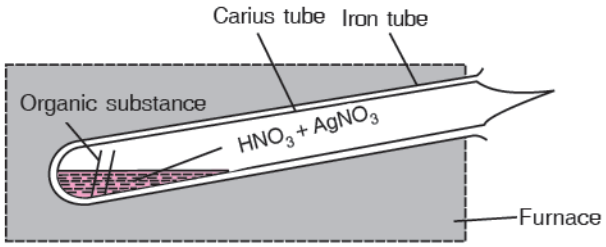

Fig. 25. Carius method for the estimation of halogens.

Calculations

Let the mass of organic compound be w g

Mass of silver halide formed = m g

Now, AgX = X

108 + X parts by weight of silver halide contain X parts by weight of halogen (X is its atomic mass).

(108 + X) g of silver halide give halogen = X

m g of silver halide will give halogen

$$= \frac{X}{(108 + X)} \times m \text{ g}$$

$\therefore$ Percentage of halogen

$$= \frac{\text{Mass of halogen}}{\text{Mass of organic compound}} \times 100$$

$$= \frac{X \times m}{(108 + X)} \times \frac{100}{w}$$

Here X is the atomic mass of halogen, e.g.
Cl = 35.5, Br = 80 (79.9 exact), I = 127 (126.9 exact)

Percentage of halogen =

$$\frac{\left(\begin{matrix}\text{Atomic mass}\\ \text{of halogen}\end{matrix}\right) \times \left(\begin{matrix}\text{Mass of}\\ \text{silver halide}\end{matrix}\right)}{\left(\begin{matrix}\text{108 + At. mass}\\ \text{of halogen}\end{matrix}\right) \times \left(\begin{matrix}\text{Mass of organic}\\ \text{substance}\end{matrix}\right)} \times 100$$

4. Estimation of Sulphur

Sulphur is estimated by **Carius method.**

Principle. A known mass of the organic compound is heated with fuming HNO_3 in a sealed tube when sulphur is quantitatively converted into sulphuric acid. It is then precipitated with barium chloride as barium sulphate. The precipitate is filtered, washed, dried and weighed. From the weight of $BaSO_4$ formed, the percentage of sulphur can be calculated. The main reactions are :

$$S + H_2O + 3O \xrightarrow{HNO_3} H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{ppt.}}{BaSO_4}$$

Procedure. About 0.2 g of organic compound is heated with about 5 cm^3 of fuming HNO_3 in a Carius tube as described under the estimation of halogens. Upon heating, carbon and hydrogen are oxidised to carbon dioxide and water vapours respectively. Sulphur changes to sulphuric acid. After heating for 5–6 hours, the heating is stopped. The Carius tube is then broken and the contents are transferred to a beaker. Barium chloride solution is now added dropwise when sulphuric acid gets precipitated as barium sulphate. The precipitate is filtered, washed, dried and is finally weighed.

Calculations :

Let the mass of organic compound = w g

Mass of $BaSO_4$ formed = m g

$BaSO_4 \equiv S$

$137 + 32 + 64 \equiv 32$

$= 233$

233 g of $BaSO_4$ contain sulphur = 32 g

m g of $BaSO_4$ will contain sulphur $= \frac{32 \times m}{233}$ g

Percentage of sulphur

$$= \frac{\text{Mass of sulphur}}{\text{Mass of organic compound}} \times 100$$

$$= \frac{32\,a}{233} \times \frac{100}{w}$$

Percentage of S =

$$\frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

5. Estimation of Phosphorus

For the estimation of phosphorus, the given organic compound is heated strongly with fuming nitric acid. The phosphorus in the compound is oxidised to phosphoric acid. It is treated with magnesia mixture (a solution containing magnesium chloride, ammonium chloride and a little of ammonia). A precipitate of magnesium ammonium phosphate $MgNH_4PO_4$ is formed. This is filtered, washed, dried and is then ignited to give magnesium pyrophosphate ($Mg_2P_2O_7$). From the weight of $Mg_2P_2O_7$, phosphorus can be estimated.

$$\underset{\text{in organic compound}}{2P} + 5O \text{ (from } HNO_3) \xrightarrow{\text{Heat}} P_2O_5$$

$$P_2O_5 + 3H_2O \xrightarrow{\text{Heat}} \underset{\text{Phosphoric acid}}{H_3PO_4}$$

$$H_3PO_4 + \underset{(NH_4Cl + MgCl_2)}{\text{Magnesia mixture}} \longrightarrow \underset{\text{(White ppt)}}{\text{Mg } NH_4PO_4}$$

Magnesium ammonium phosphate

$$2MgNH_4PO_4 \xrightarrow{\text{Heat}} \underset{\text{pyrophosphate (white ppt)}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

Magnesium

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Calculations :

Let the mass of the organic compound = w g

Mass of magnesium pyrophosphate formed = m g.

$$Mg_2P_2O_7 \equiv 2P$$
$$2 \times 24 + 2 \times 31 + 7 \times 16 \equiv 2 \times 31$$
$$= 222 \qquad 62$$

222 g of $Mg_2P_2O_7$ contain phosphorus = 62 g

$$m \text{ g of } Mg_2P_2O_7 \text{ contain phosphorus} = \frac{62}{222} \times m \text{ g}$$

$$\therefore \quad \text{Percentage of phosphorus} = \frac{\text{Mass of phosphorus}}{\text{Mass of organic compound}} \times 100$$

$$= \frac{62m}{222} \times \frac{100}{w}$$

Percentage of phosphorus

$$= \frac{62}{222} \times \frac{\text{Mass of magnesium pyrophosphate}}{\text{Mass of organic substance}} \times 100$$

Alternatively, phosphorus may also be estimated as ammonium molybdate. In this method, by heating a known mass of an organic compound with fuming acid, the phosphoric acid formed is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4.12MnO_3$ by adding ammonia and ammonium molybdate.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21\,HNO_3 \xrightarrow{\text{Heat}} \underset{\text{(Ammonium molybdate)}}{}$$
$$(NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$$
Ammonium phosphomolybdate (yellow ppt)

The precipitates of ammonium phosphomolybdate thus formed are filtered, washed, dried and weighed.

Calculations :

Let the mass of organic compound = w g

Mass of ammonium phosphomolybdate formed = m g

$$(NH_4)_3PO_4.12MoO_3 \equiv P$$
$$3(14 + 4) + 31 + 4 \times 16 + 12\,(96 + 3 \times 16) \qquad 31$$
$$= 1877 \qquad 31$$

1877 g of $(NH_4)_3PO_4.12MoO_3$ contain phosphorus = 31 g

m g of $(NH_4)_3PO_4.12MoO_3$ contain phosphorus $= \frac{31}{1877} \times m$

Percentage of phosphrus $= \frac{31m}{1877} \times \frac{100}{w}$

Percentage of phosphorus

$$= \frac{31}{1877} \times \frac{\text{Mass of amm. phosphomolybdate}}{\text{Mass of organic substance}} \times 100$$

6. Estimation of Oxygen

There is no direct method for the estimation of oxygen in a given organic compound. It is estimated by subtracting the sum of the percentages of all other elements in the compound from 100.

Percentage of oxygen

= 100 – (% of all other elements)

However, oxygen can also be estimated directly as explained below :

A definite amount of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen are passed over red hot coke when all the oxygen gets converted to carbon monoxide. The mixture is then passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidized to carbon dioxide and producing iodine. The percentage of oxygen can be calculated from the amount of carbon dioxide or iodine produced.

$$\text{Organic compound} \xrightarrow{\text{Heat}} O_2 + \text{Gaseous products}$$
$$2C + O_2 \longrightarrow \underset{\text{Carbon monoxide}}{2CO}$$
$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

Let the mass of organic compound taken = x g

Mass of carbon dioxide formed = m g

44 g of carbon dioxide contains 32 g oxygen

$$m \text{ g of carbon dioxide contains oxygen} = \frac{32 \times m}{44} \text{ g}$$

$$\therefore \quad \text{Percentage of oxygen} = \frac{32 \times m \times 100}{44 \times x}$$

These days the estimation of elements in an organic compound is done by using only micro-quantities of substances with the help of automatic experimental techniques. The elements carbon, hydrogen and nitrogen present in a compound are determined with the help of an instrument called **CHN elemental analyzer**. In this technique very small quantities (about 1–3 mg) of the substance are required and the results are obtained on a screen within a short time. The detailed discussion of these methods is beyond the scope of the present syllabus.

SOLVED EXAMPLES

Example 39.

0.15 g of an organic compound gave 0.12 g of AgBr by Carius method. Find the percentage of bromine in the compound.

Solution : Mass of AgBr formed = 0.12 *g*

$$AgBr \equiv Br$$
$$188 \qquad 80$$

188 g of AgBr contain bromine = 80 g

$$0.12 \text{ g of AgBr will contain bromine} = \frac{80 \times 0.12}{188} = 0.051 \text{ g}$$

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$$\text{Percentage of bromine} = \frac{0.051}{0.15} \times 100$$
$$= \mathbf{34.04\%}$$

❑ **Example 40.**

0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582 g of $BaSO_4$. Calculate the percentage of sulphur in the compound.

Solution :

Mass of $BaSO_4$ = 0.582 g

We know $\underset{233}{BaSO_4} \equiv \underset{32}{S}$

233 g of $BaSO_4$ contain sulphur = 32 g

0.582 g of $BaSO_4$ contain sulphur = $\frac{32}{233} \times 0.582$

$$\text{Percentage of sulphur} = \frac{\text{Wt. of sulphur}}{\text{Wt. of compound}} \times 100$$
$$= \frac{32 \times 0.582}{233 \times 0.395} \times 100 = \mathbf{20.24\%}$$

Practice Problems

◑ **28.** In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound ?

N.C.E.R.T.

◑ **29.** 0.25 g of an organic compound 'X' containing carbon, hydrogen and oxygen was analysed by the combustion method. The increase in mass of calcium chloride tube and potash bulbs at the end of the experiment was found to be 0.15 g and 0.1837 g respectively. Calculate the percentage composition of the compound.

◑ **30.** 0.2325 g of an organic compound was analysed for nitrogen by Duma's method. 31.7 mL of moist nitrogen was collected at 25°C and 755.8 mm pressure. Calculate the percentage of nitrogen in the sample (aq. tension of water at 25°C and 23.8 mm).

◑ **31.** 0.2585 g of an organic compound containing iodine was heated with excess of strong nitric acid and silver nitrate in a Carius tube. The precipitate of silver iodide was filtered, washed and dried. Its weight was found to be 0.3894 g. Calculate the percentage of iodine in the compound.

◑ **32.** 0.4 g of an organic compound was kjeldahlised and the ammonia evolved was absorbed into 50 mL of M/4 sulphuric acid solution. The residual acid solution was diluted with distilled water and the volume was made upto 150 mL. 20 mL of this diluted solution required 31 mL of M/20 NaOH solution for complete neutralisation. Calculate the percentage of nitrogen in the compound.

◑ **33.** An organic compound containing C, H, N and O gave the following results on analysis :

(*i*) 0.25 g of the compound gave 0.368 g of CO_2 and 0.205 g of H_2O

(*ii*) The same weight of the compound gave 31.2 ml of N_2 at S.T.P.

Calculate the percentage composition of the compound.

◑ **34.** 0.4 g of an organic compound containing phosphorus gave 0.555 g of magnesium pyrophosphate by usual analysis. Calculate the percentage of phosphorus in the compound.

◑ **35.** 0.12 g of an organic compound containing phosphorus gave 0.22 g of $Mg_2P_2O_7$ by usual analysis. Calculate the percentage of phosphorus in the compound.

Answers to Practice Problems

◐ **28.** 42.10%
◐ **29.** C = 20.04%, H = 6.66%, O = 73.30%
◐ **30.** 15.1%
◐ **31.** 81.4%
◐ **32.** 46.8%
◐ **33.** C = 40.14%; H = 9.11%; N = 15.6%; O = 35.15%
◐ **34.** 38.75%
◐ **35.** 51.20%

Hints & Solutions on page 119

add on CONCEPTUAL QA

Conceptual Questions 2

Q. 1. How will you separate a mixture of *o*-nitro-phenol and *p*-nitrophenol ?

Ans. A mixture of o-nitrophenol and *p*-nitrophenol can be separated by steam distillation. *o*-nitrophenol being less volatile distils over along with water while *p*-nitrophenol being non-volatile remains in the flask.

Q. 2. How will you separate benzoic acid from a mixture of naphthalene and benzoic acid ?

Ans. Benzoic acid can be separated from naphthalene by treating the mixture with hot water. Benzoic acid dissolves but naphthalene remains insoluble. On cooling, pure benzoic acid crystallises out.

Q. 3. Suggest methods for the separation of the following mixtures :

(*a*) a mixture of liquid A (b.p. 365 K) and liquid B (b.p. 355 K)

(*b*) a mixture of liquid C (b.p. 348 K) and liquid D (b.p. 478 K).

Ans. (*a*) Fractional distillation because the boiling points of the two liquids differ by only 10°.

(*b*) Simple distillation because the boiling points of the two liquids differ much.

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Q. 4. Will a precipitate of AgCl be formed on treating $CHCl_3$ with $AgNO_3$? Explain.

Ans. The precipitate of AgCl will not be formed because $CHCl_3$ is a covalent compound and does not ionize to give Cl^- ions. Therefore, $CHCl_3$ does not react with Ag^+ ions (from $AgNO_3$) to form ppt. of AgCl.

Q. 5. Name two compounds which are purified by sublimation.

Ans. Camphor, naphthalene.

Q. 6. What is the basic principle of chromatography ?

Ans. The method of chromatography is based on the difference in the rates at which the components of a mixture are adsorbed on a suitable adsorbent.

Q. 7. What conclusions would you draw if the Lassaigne's extract gives a blood red colouration with $FeCl_3$?

Ans. It indicates that the compound contains both N and S. During fusion, sodium thiocyanate is formed which gives blood red colouration.

$$3\ NaSCN + FeCl_3 \longrightarrow \underset{\text{Blood red}}{Fe(SCN)_3} + 3\ NaCl$$

CONCEPTUAL QA

Q. 8. Name a method suitable for separating the mixture of iodine and sodium chloride.

Ans. Sublimation is used to separate the mixture of iodine and sodium chloride because iodine sublimes readily.

Q. 9. Why is nitric acid added to sodium extract before ading silver nitrate solution for testing halogens ? ***N.C.E.R.T.***

Ans. Sodium extract is boiled with nitric acid to decompose NaCN and NaS if present.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$Na_2S + HNO_3 \longrightarrow 2NaNO_3 + H_2S\uparrow$$

If cyanide and sulphide ions are not decomposed, they will interfere with the test by forming precipitate of AgCN and Ag_2S.

$$NaCN + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCN} + NaNO_3$$

$$Na_2S + 2AgNO_3 \longrightarrow \underset{\substack{\text{Silver sulphide}\\ \text{(Black ppt).}}}{Ag_2S} + 2NaNO_3$$

Q. 10. Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test ?

Ans. For testing sulphur, the sodium extract is acidified with acetic acid because lead acetate is soluble and does not interfere with the test. If H_2SO_4 were used, lead acetate will react with it forming white precipitate of lead sulphate.

$$(CH_3COO)_2Pb + H_2SO_4 \longrightarrow \underset{\text{White ppt.}}{PbSO_4} + 2CH_3COOH$$

Q. 11. The R_f value of A and B in a mixture determined by TLC in a solvent mixture are 0.65 and 0.42 respectively. If the mixture is separated by column chromatography using the same solvent mixture on a mobile phase, which of the two components A or B will elute first ? Explain.

Ans. R_f value of A is 0.65, therefore, it is less strongly adsorbed as compared to compound B which has R_f value of 0.42. Therefore, A will be eluted first.

Q. 12. A mixture contains 71 per cent of calcium sulphate and 29 per cent of camphor. Name a suitable technique of separation of the components of the mixture.

Ans. The mixture can be separated by the process of sublimation. Camphor will sublime whereas calcium sulphate will be left behind.

Q. 13. Suggest a suitable technique of separating naphthalene from kerosene present in a mixture.

Ans. By differential extraction.

Q. 14. Write the molecular formula of iron (III) hexacyanidoferrate (II).

Ans. $Fe_4[Fe(CN)_6]_3$.

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SOLUTION FILE

Hints & Solutions for Practice Problems

28. Molecular mass of $BaSO_4$ = 137 + 32 + 64 = 233

233 g of $BaSO_4$ contains S = 32 g

0.4813 g of $BaSO_4$ contains S = $\frac{32}{233} \times 0.4813$ = 0.0661 g

% of Sulphur = $\frac{0.0661}{0.157} \times 100$ = **42.10%**

29. Wt. of CO_2 formed = Increase in potash bulbs = 0.1837 g

Wt. of organic compound = 0.25

$$\% C = \frac{12}{44} \times \frac{0.1837}{0.25} \times 100 = \mathbf{20.04\%}$$

Wt. of H_2O produced= Increase in $CaCl_2$ tube = 0.15 g

$$\% H = \frac{2}{18} \times \frac{0.15}{0.25} \times 100 = \mathbf{6.66\%}$$

% of O = 100 – (20.04 + 6.66) = **73.30%**

30. *Calculation of volume of nitrogen at S.T.P.*

Experimental conditions

P_1 = 755.8– 23.8 = 732.0 mm

V_1 = 31.7 mL

T_1 = 25 + 273 = 298 K

S.T.P. conditions

P_2 = 760 mm

V_2 = ?

T_2 = 273 K

Applying gas equation,

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

$$\frac{732 \times 31.7}{298} = \frac{760 \times V_2}{273}$$

or V_2 = 28 mL

$$\% \text{ of } N = \frac{28 \times \text{Volume of } N_2 \text{ at S.T.P.} \times 100}{22400 \times \text{mass of compound}}$$

$$= \frac{28 \times 28 \times 100}{22400 \times 0.2325} = \mathbf{15.1}$$

31. Wt. of organic compound = 0.2585 g

Wt. of silver iodide formed = 0.3894 g

AgI ≡ I

235 g of AgI gives iodide = 127 g

0.3894 g of AgI gives iodide = $\frac{127}{235} \times 0.3894$

$$\% \text{ of iodine} = \frac{127}{235} \times \frac{0.3894}{0.2585} \times 100 = \mathbf{81.4\%}$$

32. Volume of $\frac{N}{2}$ H_2SO_4 taken = 50 mL

Let volume of $\frac{N}{2}$ H_2SO_4 left unused = V mL

V mL of acid solution was diluted to 150 mL and titrated against N/20 NaOH

20 mL of diluted solution ≡ 31 mL of $\frac{N}{20}$ NaOH

Normality of diluted solution = $\frac{30 \times 1}{20 \times 20} = \frac{31}{400}$ N

Normality of 150 mL of acid solution = $\frac{31}{400}$ N

V mL of $\frac{N}{2}$ H_2SO_4 ≡150 mL of $\frac{31}{400}$N diluted acid

$$\therefore V = \frac{150 \times 31 \times 2}{1 \times 400} = 23.25 \text{ mL}$$

Volume of $\frac{N}{2}$ H_2SO_4 left = 23.25 mL

Volume of acid used up for ammonia = 50 – 23.25 mL = 26.75 mL

26.75 mL of $\frac{N}{2}$ H_2SO_4 ≡ 26.75 mL of $\frac{N}{2}$ NH_3 solution

Wt. of nitrogen in 26.75 mL of $\frac{N}{2}$ NH_3

$$= \frac{14}{2} \times \frac{26.75}{1000} = 0.1872 \text{ g}$$

$$\% N = \frac{0.1872}{0.4} \times 100 = \mathbf{46.8\%}$$

33. (*i*)Percentage of C

$$= \frac{12}{44} \times \frac{\text{Wt. of } CO_2}{\text{Wt. of compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.368}{0.25} \times 100 = \mathbf{40.14\%}$$

(*ii*) Percentage of H = $\frac{2}{18} \times \frac{\text{Wt. of water}}{\text{Wt. of compound}} \times 100$

$$= \frac{2}{18} \times \frac{0.205}{0.25} \times 100 = \mathbf{9.11\%}$$

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Solution File

(*iii*) Percentage of N

$$= \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at S.T.P.}}{\text{Wt. of compound}} \times 100$$

$$= \frac{28}{22400} \times \frac{31.2}{0.25} \times 100$$

$$= \mathbf{15.6\%}$$

Percentage of O = 100 – (40.14 + 9.11 + 15.60)

= **35.15%**

34.

$$\underset{62}{2P} \equiv \underset{222}{Mg_2P_2O_7}$$

$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{Wt. of } Mg_2P_2O_7}{\text{Wt. of compound}} \times 100$$

$$= \frac{62}{222} \times \frac{0.555}{0.40} \times 100 = \mathbf{38.75\%}$$

35. Wt. of organic compound = 0.12g

$$\underset{62}{2\,Mg} = \underset{222}{Mg_2P_2O_7}$$

222 g of $Mg_2P_2O_7$ contains Mg = 62

0.22 g of $Mg_2P_2O_7$ contains Mg = $\frac{62}{222} \times 0.22$

= 0.06144 g

$$\% \text{ of P} = \frac{0.06144}{0.12} \times 100 = \mathbf{51.20\ \%}$$

Chapter Summary

Key Terms

- **Homologous series:** A series of similarly constituted compounds in which the members possess the same functional group and have similar chemical characteristics.
- **Isomers:** The compounds which have the same molecular formula but differ in their physical and chemical properties.
- **Inductive effect:** The process of electron displacement along the chain of carbon atoms due to the presence of a polar covalent bond at one end of the chain.
- **Electromeric effect:** The phenomenon of movement of electrons from one atom to another in multi bonded atoms at the demand of attacking regent.
- **Resonance:** If a molecule can be represented by two or more structures, none of which is capable of describing all the known properties of the compound, then the actual structure is intermediate or resonance hybrid of these structures.
- **Hyperconjugation:** Conjugation between electrons of single (H–C) bond with multiple bonds.
- **Electrophiles:** The positively charged or neutral species which are deficient in electrons.
- **Distillation:** The process is used for the purification of liquids which boil without decomposition and contain non-volatile impurities.
- **Fractional distillation:** The process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other.
- **Steam distillation** is used for separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture.
- **Differential extraction:** The method is used to separate a given organic compound present in aqueous solution by shaking with a suitable organic solvent in which the compound is more soluble than water.
- **Chromatography:** Based on the differences in rates at which the components of a mixture are adsorbed as a suitable adsorbent.

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QUICK CHAPTER ROUND UP

ORGANIC COMPOUNDS

Homologous series
- series of similar compounds
- differ by —CH_2 group

⟺

Functional group
- determines the characteristics of a compound

⇓

ISOMERS

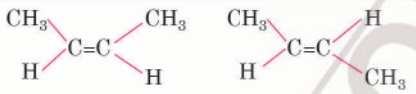
Compounds having same molecular formula but different physical and chemical properties

Structural isomerism

- **Chain or nuclear**
  $CH_3CH_2CH_2CH_3$ & $CH_3CH(CH_3)_2$
- **Position**
  $CH_3CH_2CH_2OH$ & $CH_3CH(OH)CH_3$
- **Functional**
  CH_3CH_2OH & CH_3OCH_3
- **Metamerism**
  $C_2H_5COC_2H_5$ & $CH_3COC_3H_7$
- **Tautomerism**
  $CH_3C(=O)H$ & $CH_2=CHOH$

Stereoisomerism

Geometrical



cis But-2-ene trans

Conditions
- should have double bond
- two groups attached to same C atom of double bond must be different.

Optical isomerism

Rotate the plane polarised light in different directions

Electron Displacement in Covalent Bond

Inductive effect

$\delta''_+ \quad \delta'_+ \quad \delta_+ \quad \delta_+ \quad \delta_-$

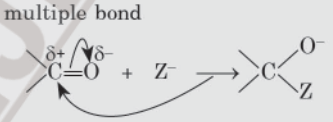
$—C \rightarrow C \rightarrow C \rightarrow C \rightarrow Cl$

$\delta'''_+ < \delta''_+ < \delta'_+ < \delta_+$

–I :$–NO_2$ > –CN > –COOH > –COOR >
F > Cl > Br > OH > $–OCH_3$ > C_6H_5 > H

+I :$–(CH_3)_3C–$ > $(CH_3)_2CH–$ > $CH_3CH_2–$ > $CH_3–$

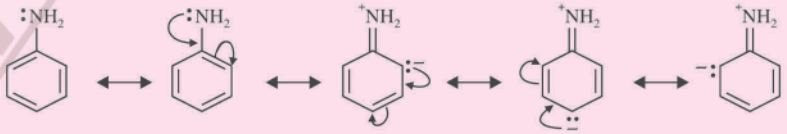
Electromeric effect
- occurs between two atoms joined by multiple bond



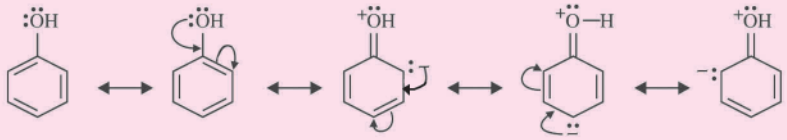
Hyperconjugation
- interaction between electrons of π system and adjacent σ bonds (single H—C bonds).

Resonance

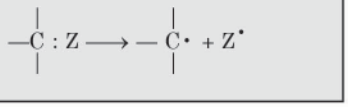
Aniline $C_6H_5NH_2$:



Phenol C_6H_5OH :

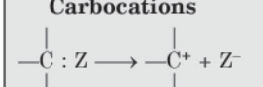


Homolytic fission gives free radicals

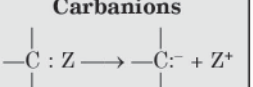


Heterolytic fission gives

Carbocations



Carbanions



Free radicals
Planar : sp^2 hybridised carbon

$\dot{C}H_3 < 1° < 2° < 3°$

Carbocations
Planar : sp^2 hybridised C

$3° > 2° > 1° > CH_3^+$

$(C_6H_5)_3C^+ > (C_6H_5)_2CH^+ > (C_6H_5)CH_2^+$

Carbanions
Pyramidal : sp^3 hybridised C

$CH_3^- > 1° > 2° > 3°$

$(C_6H_5)_3C^- > (C_6H_5)_2CH^- > C_6H_5CH_2^-$

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Methods of Purification

- **Filtration**
  ⇒ mixture of naphthalene and urea
- **Recrystallisation**
  ⇒ sugar containing common salt
- **Sublimation**
  ⇒ purification of camphor
- **Distillation**
  ⇒ separation of $CHCl_3$ and aniline
- **Fractional distillation**
  ⇒ acetone and methanol
- **Steam distillation**
  ⇒ o-nitrophenol and *p*-nitrophenol
- **Differential extraction**
  ⇒ aniline and water
- **Chromatography**
  ⇒ ortho and para nitroanilines

Lassaigne's test is used for detection of nitrogen, halogen and sulphur.

Estimation of Elements

$$\%\ C = \frac{12}{44} \times \frac{\text{Mass of } CO_2}{\text{Mass of compound}} \times 100$$

$$\%\ H = \frac{2}{18} \times \frac{\text{Mass of } H_2O}{\text{Mass of compound}} \times 100$$

$$\%\ N = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at STP}}{\text{Mass of compound}} \times 100 \textbf{ (Duma's method)}$$

$$= \frac{1.4 \times \text{Molarity of acid} \times \text{Basicity} \times \text{Vol. of acid used}}{\text{Mass of compound}} \times 100 \textbf{ (Kjeldahl's method)}$$

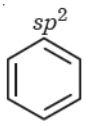
$$\%\ X_{(\text{halogen})} = \frac{\text{At. mass of X} \times \text{Mass of AgX}}{(108 + \text{At. mass of X}) \times \text{Mass of compound}} \times 100$$

$$\%\ S = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4}{\text{Mass of compound}} \times 100$$

NCERT FILE Solved

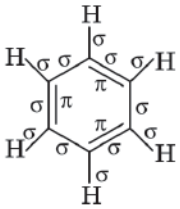
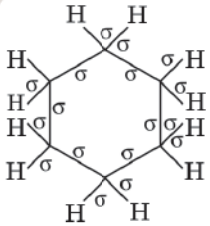
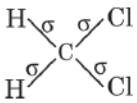
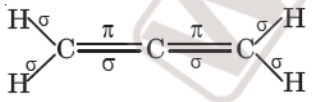
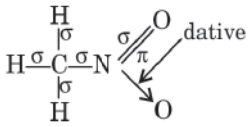
NCERT Textbook Exercises

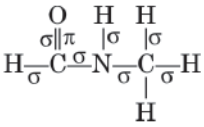
Q. 1. What are hybridisation states of each carbon atom in the following compounds?
$CH_2{=}C{=}O$, $CH_3CH{=}CH_2$, $(CH_3)_2CO$, $CH_2{=}CHCN$, C_6H_6

Ans. $\overset{sp^2}{CH_2} = \overset{sp}{C} = O$, $\overset{sp^3}{CH_3}\overset{sp^2}{CH} = \overset{sp^2}{CH_2}$, $\overset{sp^3}{CH_3}-\overset{sp^2}{\underset{\underset{O}{\|}}{C}}-\overset{sp^3}{CH_3}$, $\overset{sp^2}{CH_2} = \overset{sp^2}{CH}\overset{sp}{CN}$, 

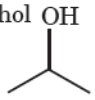
each C is sp^2 hybridised.

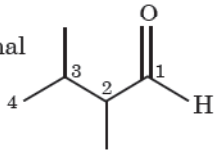
Q. 2. Indicate the σ and π bonds in the following molecules :
C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2 = C = CH_2$, CH_3NO_2, HCONHCH$_3$

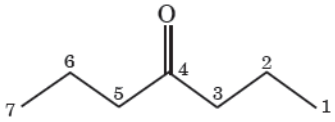
Ans. 







Q. 3. Write bond line formulas for : Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4-one.

Ans. (*i*) Isopropylalcohol 

(*ii*) 2, 3-Dimethylbutanal 

(*iii*) Heptan-4-one 

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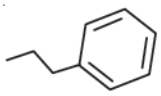
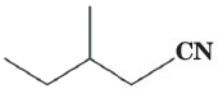
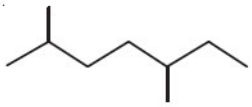
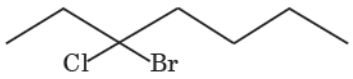
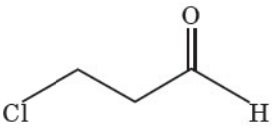
Q. 4. Give the IUPAC names of the following compounds :

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*e*) 

(*f*) Cl_2CHCH_2OH

Ans. (*a*) Propylbenzene (*b*) 3-Methylpentanenitrile (*c*) 2, 5-Dimethylheptane

(*d*) 3-Bromo-3-chloroheptane (*e*) 3-Chloropropanal (*f*) 2,2-Dichloroethanol

Q. 5. Which of the following represents the correct IUPAC name for the compounds concerned ?

(*a*) 2,2-Dimethylpentane or 2-Dimethylpentane (*b*) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane

(*c*) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane (*d*) But-3-yn-1-ol or But-4-ol-1-yne.

Ans. (*a*) 2,2-Dimethylpentane (*b*) 2,4,7-Trimethyloctane (*c*) 2-Chloro-4-methylpentane (*d*) But-3-yn-1-ol

Q. 6. Draw formulas for the first five members of each homologous series beginning with the following compounds.

(*a*) H—COOH **(*b*) CH_3COCH_3** **(*c*) $H—CH=CH_2$**

Ans. *Please try yourself.*

Q. 7. Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for :

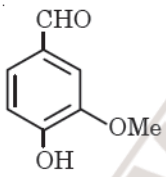
(*a*) 2,2,4-Trimethylpentane

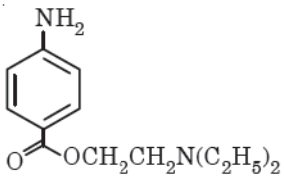
(*b*) 2-Hydroxy-1,2,3-propanetricarboxylic acid

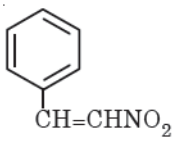
(*c*) Hexanedial

Ans. *Refer Solved Example 18. (Page 63)*

Q. 8. Identify the functional groups in the following compounds :

(*a*) 

(*b*) 

(*c*) 

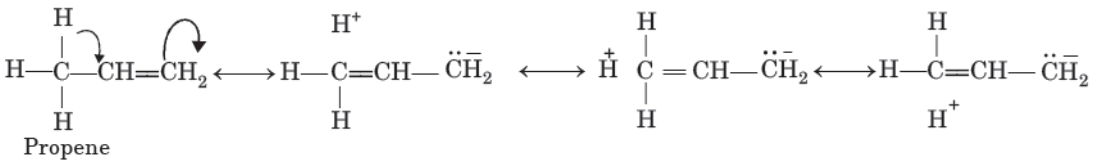
Ans. *Refer Solved Example 19. (Page 64)*

Q. 9. Which of the two : $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why ?

Ans. *Refer Conceptual Questions* 1, *Q.20 (page 96)*

Q. 10. Explain why alkyl groups act as electron donors when attached to a π system.

Ans. Alkyl groups act as electron donors when attached to a π-system because of hyperconjugation as shown below :



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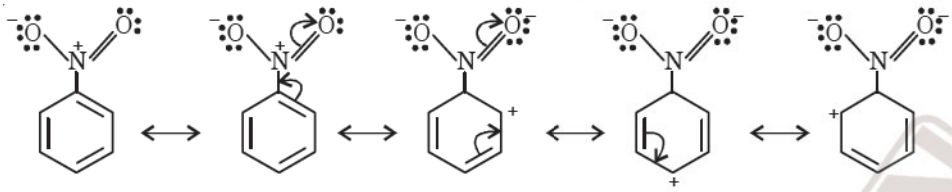
Q. 11. Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation

(*a*) C_6H_5OH (*b*) $C_6H_5NO_2$ (*c*) $CH_3CH{=}CHCHO$ (*d*) $C_6H_5{-}CHO$ (*e*) $C_6H_5{-}\overset{+}{C}H_2$ (*f*) $CH_3CH{=}\overset{+}{C}HCH_2$

Ans. For parts (*a*), (*d*) and (*e*) *Refer Conceptual Questions* 1, *Q.24 (Page 97).*

(*b*)



(*c*) $CH_3{-}CH{=}CH{-}CH{=}\ddot{O}: \longleftrightarrow CH_3{-}CH{=}CH{-}\overset{+}{C}H{-}\ddot{O}:^- \longleftrightarrow CH_3{-}\overset{+}{C}H{-}CH{=}CH{-}\ddot{O}:^-$

(*d*) $CH_3{-}CH{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow CH_3{-}\overset{+}{C}H{-}CH{=}CH_2$

Q. 12. What are electrophiles and nucleophiles? Explain with examples.

Ans. The positively charged or neutral species which are deficient of electrons and can accept a pair of electrons are called electrophiles. For example, H_3O^+, Cl^+, NO_2^+, BF_3, $AlCl_3$, etc.

The species having an atom having unshared or lone pair of electrons and seeking positive sites are called nucleophiles.

For example, NH_3, H_2O, ROR, CN^-, X^-, etc.

Q. 13. Identify the reagents shown underlined in the following equations as nucleophiles or electrophiles :

(*a*) $CH_3COOH + \underline{HO^-} \longrightarrow CH_3COO^- + H_2O$ (*b*) $CH_3COCH_3 + \underline{\bar{C}N} \longrightarrow (CH_3)_2C(CN)(OH)$

(*c*) $C_6H_5 + \underline{\overset{+}{C}H_2CO} \longrightarrow C_6H_5COCH_3$

Ans. *Refer Solved Example 30. (Page 92)*

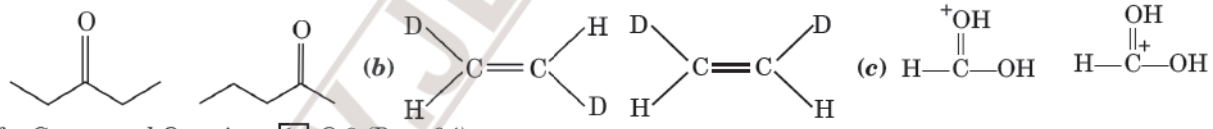
Q. 14. Classify the following reactions in one of the reaction type studied in this unit.

(*a*) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$ (*b*) $(CH_3)_2C{=}CH_2 + HCl \longrightarrow (CH_3)_2ClC{-}CH_3$

(*c*) $CH_3CH_2Br + HO^- \longrightarrow CH_2{=}CH_2 + H_2O + Br^-$ (*d*) $(CH_3)C{-}CH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$

Ans. *Refer Solved Example 29. (Page 91)*

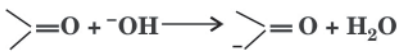
Q. 15. What is the relationship between the members of following pairs of structures ? Are they structural or geometrical isomers or resonance contributors ?

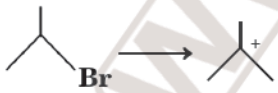


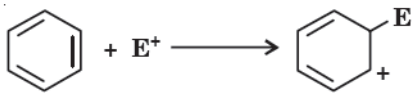
Ans. *Refer Conceptual Questions* 1, *Q.8 (Page 94)*

Q. 16. For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

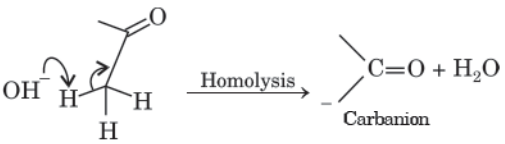
(*a*) $CH_3O{-}OCH_3 \longrightarrow CH_3\dot{O} + \dot{O}CH_3$

(*b*) 

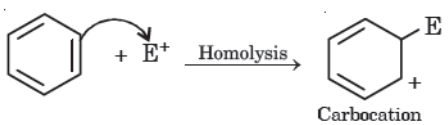
(*c*) 

(*d*) 

Ans. (*a*) $CH_3O{-}OCH_3 \xrightarrow{\text{Homolysis}} CH_3\dot{O} + \dot{O}CH_3$

(*b*) 

(*c*)

(*d*) 

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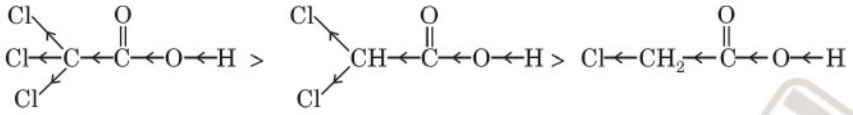
Q. 17. Explain the terms Inductive and Electromeric effects. Which electron displacement effect explain the following correct orders of acidity of the carboxylic acids ?

(*a*) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$ (*b*) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

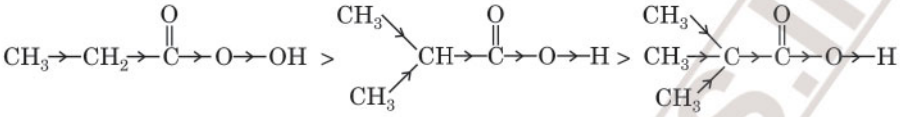
Ans. For definition *Refer Text. (Page 72-73, 77)*

(*a*) As the number of halogen atoms decreases, the overall –I effect decreases so that the tendency to withdraw electrons from O—H bond decreases. Consequently, acidic character decreases.



Inductive effect (–I) decreases.

(*b*) As the number of alkyl groups increases, the +I effect increases and therefore, acid strength decreases.



+I effect increase

Q. 18. Give a brief description of the principles of the following techniques taking an example in each case.

(*a*) Crystallisation (*b*) Distillation (*c*) Chromatography

Ans. *Refer Text. (Page 99, 100, 104)*

Q. 19. Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

Ans. Two compounds with different solubilities in a solvent S can be separated by fractional crystallisation. When a hot saturated solution of these two compounds is allowed to cool, the less soluble compound crystallises out first while the other more soluble compound remains in the solution. The crystals of less soluble compound are separated from the mother liquor. The mother liquor is again concentrated and the hot solution is again allowed to cool when the crystals of second (*i.e.,* more soluble) compound are obtained. These compounds are again filtered and dried.

Q. 20. What is the difference between distillation, distillation under reduced pressure and steam distillation?

Ans. **Distillation** means the conversion of a liquid into vapours, which on condensation by cooling gives a pure liquid. This method is used for purification of liquids which boil without decomposition and contain non-volatile impurities. This method can also be used for separating liquids having sufficient differences in their boiling points.

Distillation under reduced pressure also involves conversion of a liquid into vapours by heating followed by condensation of the vapours thus produced by cooling under reduced pressure. In this method, the pressure acting on the system is not atmospheric pressure but is reduced with help of a vacuum pump. This method is used to purify liquids which decompose below their normal boiling points.

Steam distillation is similar to distillation under reduced pressure even though there is no reduction in the total pressure acting on the solution. It is used for the separation and purification of a liquid which is appreciably volatile in steam from non-volatile components of a mixture. The mixture of organic liquid and water boils at a temperature when the sum of the vapour pressure of the organic liquid (p_1) and that of water (p_2) becomes equal to atmospheric pressure i.e., $(p) = p_1 + p_2$.

Q. 21. Discuss the chemistry of Lassaigne's test. ?

Ans. *Refer Text Page 107.*

Q. 22. Differentiate between the principle of estimation of nitrogen in an organic compound by (*i*) Dumas method and (*ii*) Kjeldahl's method

Ans. In Dumas method, a known mass of an organic compound is heated with excess of CuO in an atmosphere of CO_2 when nitrogen of the organic compound is converted into N_2 gas. The volume of N_2 thus obtained is converted into N.T.P. and percentage of nitrogen is calculated by using the relation :

$$\%N = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at N.T.P.}}{\text{Mass of substance}} \times 100$$

In Kjeldahl's method, a known mass of an organic compound is heated with conc. H_2SO_4 in the presence of K_2SO_4(raises the b.p. of H_2SO_4) and little $CuSO_4$ or Hg (catalyst) in a Kjeldahl's flask when nitrogen present in the compound is quantitatively converted into $(NH_4)_2SO_4$. The $(NH_4)_2SO_4$ thus obtained is boiled with excess of NaOH solution to liberate NH_3 gas which is absorbed in a known excess of standard solution of H_2SO_4 or HCl. The volume of acid unused is determined by titration against a standard alkali solution. From the volume of acid used, the percentage of N is calculated from the relation :

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$$\% \text{ N} = \frac{1.4 \times \text{ Molarity of acid } \times \text{ Basicity of acid } \times \text{Vol. of acid used}}{\text{Mass of substance taken}}$$

Q. 23. Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

Ans. *Refer Text page 114, 115.*

Q. 24. Explain the principle of paper chromatography.

Ans. *Refer Text page 106.*

Q. 25. Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens ?

Ans. *Refer Conceptual Questions* 2, *Q. 9 (page 118).*

Q. 26. Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

Ans. The organic compound is fused with sodium metal to convert these elements (N, S or halogens) present in the covalent compound to ionic form.

Q. 27. Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Ans. A mixture of $CaSO_4$ and camphor can be separated by the following two methods :

(*i*) Camphor is sublimable while $CuSO_4$ is not sublimable. Hence, the mixture can be sublimed to get camphor.

(*ii*) Camphor is soluble in organic solvents such as CCl_4, $CHCl_3$, etc. while $CaSO_4$ is not soluble. Therefore, when the mixture is shaken with a solvent, camphor goes into the solution while $CaSO_4$ remains as residue. It is filtered and evaporation of the filtrate gives camphor.

Q. 28. Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation?

Ans. In steam distillation, water and organic substance vaporise together and total vapour pressure becomes equal to atmospheric pressure i.e.,

Vapour pressure of organic substance + Vapour pressure of water = Atmospheric pressure.

This means that the organic compound vaporises and gets distilled at lower temperature than its boiling point.

Q. 29. Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate ? Give reason for your answer.

Ans. The precipitate of AgCl will not be formed because CCl_4 is covalent compound and does not ionise to give Cl^- ions to react with $AgNO_3$. $CCl_4 + AgNO_3 \longrightarrow$ No reaction.

Q. 30. Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound ?

Ans. Carbon dioxide is acidic and it reacts with strong base KOH to form potassium carbonate.

$$2KOH + CO_2 \longrightarrow K_2CO_3$$

This results in increase in mass of potassium hydroxide. From the increase in mass of CO_2 produced, the amount of carbon in the organic compound can be calculated by using the formula:

$$\% \text{ Carbon} = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ produced}}{\text{Mass of substance}} \times 100$$

Q. 31. Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

Ans. *Refer Conceptual Questions* 2 *Q. 10 (page 118)*

Q. 32. An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

Ans. *Refer Solved Example 31. (Page 110)*

Q. 33. A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

Ans. *Refer Solved Example 37. (Page 114)*

Q. 34. 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

Ans. Mass of substance taken = 0.3780 g

Mass of AgCl formed = 0.5740 g

$$\underset{143.5}{AgCl} \equiv \underset{35.5}{Cl}$$

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143.5 g of AgCl will contain Cl = 35.5 g

$$0.5740 \text{ g of AgCl contain Cl} = \frac{35.5}{143.5} \times 0.5740$$
$$= 0.142 \text{ g}$$

$$\% \text{ Chlorine} = \frac{0.142 \times 100}{0.3780} = \mathbf{37.57\%}$$

Q. 35. In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668g of barium sulphate. Find out the percentage of sulphur in the given compound.

Ans. Mass of organic compound = 0.468 g

Mass of $BaSO_4$ formed = 0.668 g

$BaSO_4 \equiv S$

233 32

233 g of $BaSO_4$ contains S = 32 g

$$0.668 \text{ g of } BaSO_4 \text{ contains S} = \frac{32}{233} \times 0.668$$
$$= 0.0917 \text{ g}$$
$$\% \text{ of sulphur} = \frac{0.0917}{0.468} \times 100$$
$$= 19.59\ \%$$

Q. 36. In the organic compound $CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$, the pair of hybridised orbitals involved in the formation of : $C_2{-}C_3$ bond is :

(*a*) *sp*—*sp*^{2} (*b*) *sp*—*sp*^{3} (*c*) *sp*^{2}—*sp*^{3} (*d*) *sp*^{3}—*sp*^{3}

Ans. When both double bond and triple bond are present in the molecule, the double bond is given preference in numbering as

$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH_2}{-}\overset{4}{CH_2}{-}\overset{5}{C}{\equiv}\overset{6}{CH}$$

$\therefore$ $C_2{-}C_3$ bond is formed by sp^2—sp^3

Option (c) is correct.

Q. 37. In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of :

(*a*) $Na_4[Fe(CN)_6]$ **(*b*) $Fe_4[Fe(CN)_6]_3$**

(*c*) $Fe_2[Fe(CN)_6]$ **(*c*) $Fe_3[Fe(CN)_6]_4$**

Ans. (*b*) Prussion blue colour is due to the formation of $Fe_4[Fe(CN)_6]_3$.

Q. 38. Which of the following carbocation is most stable ?

(*a*) $(CH_3)_3C.\overset{+}{C}H_2$ **(*b*) $(CH_3)_3\overset{+}{C}$**

(*c*) $CH_3CH_2\ \overset{+}{C}H_2$ **(*d*) $CH_3\overset{+}{C}H\ CH_2CH_3$**

Ans. Correct choice (b) because order of stability of carbocation is 3° > 2° > 1°.

Q. 39. The best and latest technique for isolation, purification and separation of organic compound is

(*a*) Crystallisation **(*b*) Distillation**

(*c*) Sublimation **(*d*) Chromatography**

Ans. (*d*) : Chromatography is the latest technique for isolation, purification and separation of organic compound.

Q. 40. The reaction : $CH_3CH_2I + KOH(aq) \longrightarrow CH_3CH_2OH + KI$

(*a*) electrophilic substitution **(*b*) nucleophilic substitution**

(*c*) elimination **(*d*) addition**

Ans. Correct choice is (*b*).

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NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 150.*

Short Answer Questions *Carrying 2 or 3 marks*

Note: **Consider structures I to VII and answer the questions 1 — 4.**

I. $CH_3—CH_2—CH_2—CH_2—OH$

II. $CH_3—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

III. $CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}—CH_3$

IV. $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—OH$

V. $CH_3—CH_2—O—CH_2—CH_3$

VI. $CH_3—O—CH_2—CH_2—CH_3$

VII. $CH_3—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

Q. 1. Which of the above compounds form pairs of metamers ?

Ans. V and VI or V and VII form pair of metamers because they differ only in the number of carbon atoms on the either side of the ether functional group.

Q. 2. Identify the pairs of compounds which are functional group isomers.

Ans. I and V, I and VI, I and VII, II and V, II and VI, II and VII; III and V, III and VI, III and VII; IV and V, IV and VI and IV and VII are functional isomers.

Q. 3. Identify the pairs of compounds that represent position isomerism.

Ans. I and II, III and IV and VI and VII.

Q. 4. Identify the pairs of compounds that represent chain isomerism.

Ans. I and III, I and IV, II and III and II and IV.

Q. 5. For testing halogens in an organic compound with $AgNO_3$ solution, sodium extract (Lassaigne's test) is acidified with dilute HNO_3. What will happen if a student acidifies the extract with dilute H_2SO_4 in place of dilute HNO_3 ?

Ans. White ppt of Ag_2SO_4 will be formed and the student may be mistaken for white ppt. of AgCl due to the presence of Cl.

Q. 6. What is the hybridisation of each carbon in $H_2C = C = CH_2$.

Ans. $sp^2 - sp - sp^2$.

Subjective Questions

Q. 7. Explain, how is the electronegativity of carbon atoms related to their state of hybridisation in an organic compound ?

Ans. Electronegativity increases as *s* character of the hybridised carbon increases. Therefore, the oder of electronegativity is $sp^3 < sp^2 < sp$.

Q. 8. Show the polarisation of carbon-magnesium bond in the following structure.

$$CH_3—CH_2—\overset{\delta-}{CH_2}—\overset{\delta+}{CH_2}—Mg—X$$

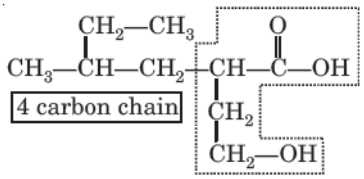
Ans. $CH_3—CH_2—CH_2—CH_2 \leftarrow Mg—X$

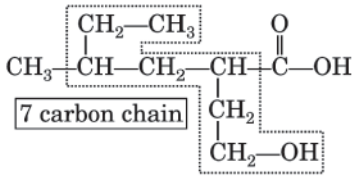
Q. 9. Compounds with same molecular formula but differing in their structures are said to be structural isomers. What type of structural isomerism is shown by

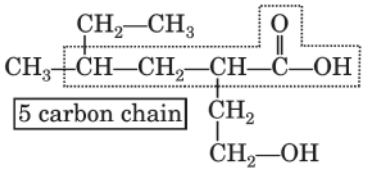
$$CH_3—S—CH_2—CH_2—CH_3 \text{ and } CH_3—S—CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

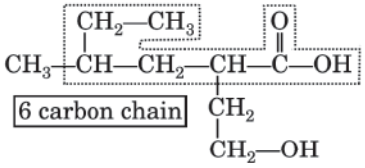
Ans. Position isomers.

Q. 10. Which of the following selected chains is correct to name the given compound according to IUPAC system.









Ans. The selected chain containing four carbon atoms is correct because it contains both the functional groups *i.e.*, —COOH (carboxyl) and —OH (hydroxyl)

Q. 11. In DNA and RNA, nitrogen atom is present in the ring system. Can Kjeldahl method be used for the estimation of nitrogen present in these ? Give reasons.

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Ans. DNA and RNA have nitrogen in the heterocyclic rings. Nitrogen present in the rings (azo group or nitro group) cannot be completely converted to ammonia. Therefore, Kjeldahl method cannot be used to estimate nitrogen present in DNA and RNA.

Q. 12. If a liquid compound decomposes at its boiling point, which method (s) can you choose for its purification. It is known that the compund is stable at low pressure, steam volatile and insoluble in water.

Ans. It can be purified by steam distillation.

Note : Answer the questions 13 to 16 on the basis of information given below :

"Stability of carbocations depends upon the electron releasing inductive effect of groups adjacent to positively charged carbon atom involvement of neighbouring groups in hyperconjugation and resonance."

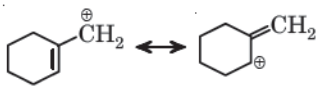
Q. 13. Draw the possible resonance structures for $CH_3-\ddot{O}-\overset{+}{C}H_2$ and predict which of the structures is more stable. Give reason for your answer.

Ans. $CH_3-\ddot{O}-\overset{+}{C}H_2 \longleftrightarrow CH_3-\overset{+}{\ddot{O}}=CH_2$

(I) (II)

Structure II is more stable because every atom has complete octet of electrons.

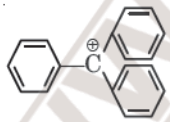
Q. 14. Which of the following ions is more stable ? Use reasonance to explain your answer.



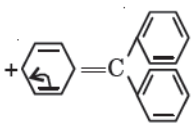
A B

Ans. Out of these two structures, structure A is more stable than B. This is because, there is resonance in structure A but no resonance is possible in structure B.

Q. 15. The structure of triphenylmethyl cation is given below. This is very stable and some of its salts can be stored for months. Explain the cause of high stability of this cation.



Ans. Due to resonance, the positive charge can move at both the *o*-and *p*-positions of each benzene ring and therefore, nine canonical structures are possible.

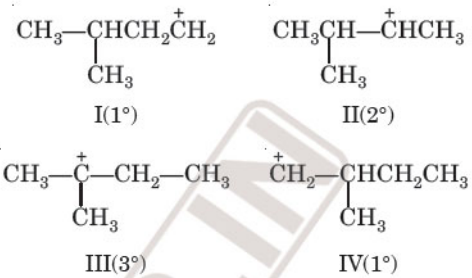


Other canonical structures

Q. 16. Write structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.

Ans. $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

The possible carbocations are :



I(1°) II(2°)

III(3°) IV(1°)

Stability of carbocations decreases in the order : 3° > 2° > 1°. Out of (IV) and I (both 1°), the electron withdrawing group of CH_3 (+I) effect, decreases with distance and therefore, carbocation (IV) is more stable than carbocation (I).

Order of increasing stability I < IV < II < III.

Q. 17. Three students, Manish, Ramesh and Rajni were determining the extra elements present in an organic compound given by their teacher. They prepared the Lassaigne's extract (L.E.) independently by the fusion of the compound with sodium metal. Then they added solid $FeSO_4$ and dilute sulphuric acid to a part of Lassaigne's extract. Manish and Rajni obtained prussian blue colour but Ramesh got red colour only. They were surprised and went to their teacher and told him about their observation. Teacher asked them to think over the reason for this. Can you help them by giving the reason for this observation. Also, write the chemical equations to explain the formation of compounds of different colours.

Ans. In Lassaigne's test, SCN^- ions are formed due to the presence of sulphur and nitrogen both. These give red colour with Fe^{3+} ions.

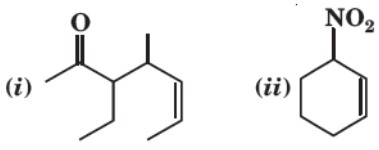
$$Fe^{3+} + 3NaSCN \longrightarrow \underset{\text{Ferric thiocyanate (Red colouration)}}{Fe(SCN)_3} + 3Na^+$$

This happens when fusion is not carried out in the excess of sodium. However, if excess of sodium metal is used, the sodium thiocyanate initially formed decomposes to form sodium cyanide and sodium sulphide as :

$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

Sodium cyanide formed gives prussian blue colour due to the formation of ferric ferrocyanide or iron (III) hexacyanoferrate (II), $Fe_4[Fe(CN)_6]_3$.

Q. 18. Name the following compounds :



(*i*) (*ii*)

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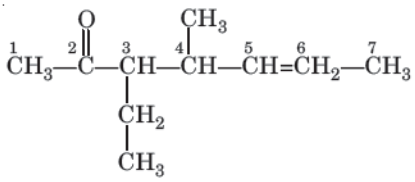
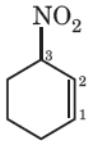
Ans. (*i*) 

3-Ethyl-4-methylhept-5-en-2-one

(*ii*)  : 3-Nitrocyclohex-1-ene

Q. 19. Write structural formulae for the following :

(*i*) 1-Bromoheptane

(*ii*) 5-Bromoheptanoic acid

Ans. (*i*) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2Br$

(*ii*) $CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_2 - CH_2 - CH_2 - COOH$

Q. 20. Draw the resonance structures of the following compounds :

(*i*) $CH_2 = CH - Cl$: (*ii*) $CH_2 = CH - CH = CH_2$

(*iii*) $CH_2 = \underset{\displaystyle H}{\underset{|}{CH}} - C = O$

Ans. (*i*) $CH_2 = CH - \ddot{Cl}: \longleftrightarrow \bar{C}H_2 - CH = \overset{+}{Cl}:$

(*ii*) $CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH - \bar{C}H_2$

(*iii*) $CH_2 = CH - \underset{\displaystyle O}{\underset{\|}{C}} - H \longleftrightarrow \overset{+}{C}H_2 - CH = \underset{\displaystyle :\ddot{O}:}{\underset{|}{C}} - H$

Q. 21. Identity the most stable species in the following sets of ions giving reasons :

(*i*) $\overset{+}{C}H_3$, $\overset{+}{C}H_2Br$, $\overset{+}{C}HBr_2$, $\overset{+}{C}Br_3$

(*ii*) $\bar{C}H_3$, $\bar{C}H_2Cl$, $\bar{C}HCl_2$, $\bar{C}Cl_3$

Ans. (*a*) $\bar{C}$–Cl_3 is most stable because Cl is more electronegative than hydrogen. On replacing hydrogen by chlorine, negative charge on C is reduced and the species becomes stable.

(*b*) $\overset{+}{C}H_3$ is most stable. The replacement of H by Br increases positive charge on carbon atom because Br is more electronegative than H and consequently the species becomes less stable.

Q. 22. Give three points of differences between inductive effect and resonance effect.

Ans. *Refer (Text Page 78)*

Q. 23. Which of the following compounds will not exist as resonance hybrid. Give reason for your answer :

(*i*) CH_3OH (*ii*) $R-CONH_2$

(*iii*) $CH_3CH = CHCH_2NH_2$

Ans. (*i*) CH_3OH : It does not contain π-electrons and therefore, cannot exist as resonance hybrid.

(*ii*) $CH_3CH = CH\ CH_2\ NH_2$ does not contain lone pair of electrons on the N atom in conjugation with the π-electrons of the double bond. Therefore, resonance is not possible.

Q. 24. Why does SO_3 act as an electrophile ?

Ans. Three highly electronegative oxygen atoms are attached to sulphur atom. This makes sulphur atom electron deficient. Due to resonance also, sulphur acquires positive charge. Both these factors make SO_3 an electrophile.

Q. 25. Which of the following resonance structure for propenal is more stable ?

$$\underset{\text{(A)}}{CH_2 = CH - CH = O} \longleftrightarrow \underset{\text{(B)}}{\overset{+}{C}H_2 - CH = CH - \bar{O}}$$

Ans. $\underset{\text{(A)}}{CH_2 = CH - CH = O} \longleftrightarrow \underset{\text{(B)}}{\overset{+}{C}H_2 - CH = CH - \bar{O}}$

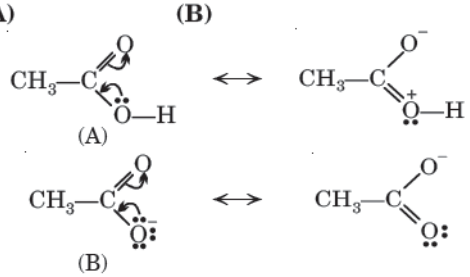
A is more stable than B.

Q. 26. By mistake, an alcohol (boiling point 97°C) was mixed with a hydrocarbon (boiling point 68°C). Suggest a suitable method to separate the two compounds. Explain the reason for your choice.

Ans. Simple distillation can be used because the two compounds have a difference of more than 20° in their boiling points and therefore, both the liquids can be distilled without any decomposition.

Q. 27. Which of the two structures (A) and (B) given below is more stabilised by resonance? Explain.

$\underset{\text{(A)}}{CH_3COOH}$ and $\underset{\text{(B)}}{CH_3CO\overset{\ominus}{O}}$

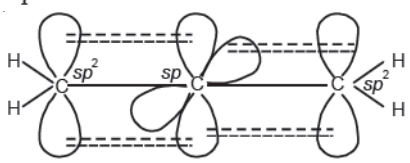
Ans. 

Structure B is more stable because it does not involve charge separation.

Long Answer Questions *Carrying 5 marks*

Q. 28. What is meant by hybridisation ? Compound $CH_2 = C = CH_2$ contains *sp* or sp^2 hybridised carbon atoms. Will it be a planar molecule ?

Ans. For hybridisation, refer units 5. No, this molecule is not a planar molecule.



Central carbon atom is *sp* hybridised and its two unhybridised *p*-orbitals are perpendicular to each other. The *p*-orbitals in one plane overlap with one

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of the *p*-orbitals of left terminal carbon atom and the *p*-orbital in other plane overlaps with *p*-orbital of right side terminal carbon atom. As a result, the position of two terminal carbon atoms and the hydrogen atoms attached to them are fixed in planes perpendicular to each other. Therefore, the pair of hydrogen atoms attached to terminal carbon atoms are present in different planes and hence molecule is not planar.

Q. 29. Benzoic acid is an organic compound. Its crude sample can be purified by crystallisation from hot water. What characteristic differences in the properties of benzoic acid and the impurity make this process of purification suitable ?

Ans. Benzoic acid can be purified from hot water because of the following characteristics :

(*i*) Benzoic acid is more soluble in hot water but less soluble in cold water.

(*ii*) Impurities present in benzoic acid are either insoluble in water or are more soluble in water to such an extent that when a hot saturated solution of benzoic acid is cooled, the impurities remain in the solution. Since impure benzoic acid satisfies both these conditions, it can be purified by crystallization.

Q. 30. Two liquids (A) and (B) can be separated by the method of fractional distillation. The boiling point of liquid (A) is less than boiling point of liquid (B). Which of the liquids do you expect to come out first in the distillate ? Explain.

Ans. *Refer Text*, fractional distillation page 101.

Liquid A with lower boiling point will distil first and liquid B with higher boiling point afterwards.

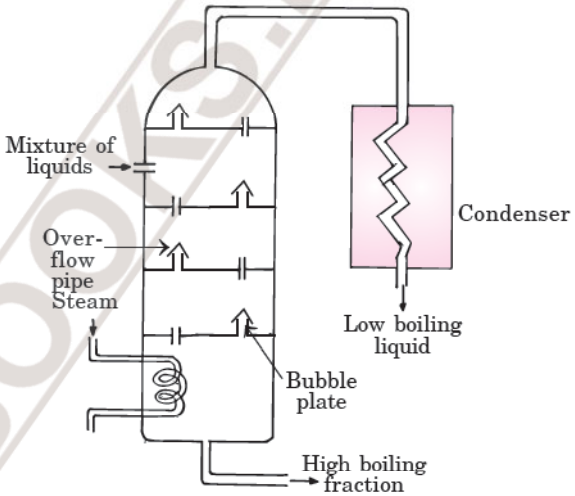
Q. 31. You have a mixture of three liquids A, B and C. There is a large difference in the boiling points of A and rest of the two liquids *i.e.*, B and C. Boiling points of liquids B and C are quite close. Liquid A boils at a higher temperature than B and C and boiling point of B is lower than C. How will you separate the components of the mixture. Draw a diagram showing set up of the apparatus for the process.

Ans. Since the boiling point of liquid A is much higher than those of liquids B and C whose boiling points are quite close, therefore, liquid A will be separated by simple distillation using the apparatus as shown in Fig. 11. Since the boiling points of liquids B and C are quite close but are much lower than that of liquid A, therefore, mixture of liquids B and C will distil together leaving behind liquid A. On further heating, liquid A will distil over.

Liquid B and C will be separated by fractionating column (Fig. 13). On fractional distillation, liquid B will distil over first and then liquid C.

Q. 32. Draw a diagram of bubble plate type fractionating column. When do we require such type of a column for separating two liquids. Explain the principle involved in the separation of components of a mixture of liquids by using fractionating column. What industrial applications does this process have?

Ans. The bubble plate type fractionating column is shown below :



In this, the long tower is divided into a number of compartments by means of shelves having openings. The openings are covered with caps called bubble caps. Each shelf has an overflow pipe which keeps the liquid to a certain level and then allows the extra liquid to trickle down to the lower shelf. This type of column is used for continuous separation of bulk quantities of liquids. For example, this method is used for distillation of fermented liquid for the manufacture of rectified spirit.

Principle of fractional distillation. *Refer Text Page 101.*

Applications (*i*) It is used to separate different fractions of crude oil in petroleum industry such as gasoline, diesel oil, kerosene oil, lubricating oil, etc.

(*ii*) It can be used for the separation of acetone and methanol from pyroligneous acid obtained by destructive distillation of wood.

Q. 33. A liquid with high boiling point decomposes on simple distillation but it can be steam distilled for its purification. Explain how is it possible ?

Ans. Refer steam distillation, *Text, Page 102.*

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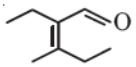
QUICK MEMORY TEST

A. Say True or False

1. Hexane has four structural isomers.
2. In $CH_2=C=CH_2$, all the carbon atoms are sp^2 hybridised.
3. Sulphur in an organic compound can be estimated by Dumas method.
4. $(CH_3)_3C^+$ is more stable than $CH_3CH_2^+$.
5. $-NO_2$ group has –I (inductive) effect.
6. Amides and oximes show functional isomerism.
7. The functional isomer of methylmethanoate is propanoic acid.
8. The IUPAC name of  is 2-Ethyl-3-methylpent-2-en-1-al.
9. Acetone (b.p. 329K) and methyl alcohol (b.p. 338K) can be separated by simple distillation.
10. In Lassaigne's test, prussian blue colour indicates the presence of nitrogen in an organic compound.

B. Complete the missing links

1. Aldehydes and ketones are ..... isomers.
2. Bond angle ..... with increase in *s*-character of the hybridised orbital.
3. Among isomeric butenes, ... is the most stable.
4. If both N and S are present in an organic compound, ... colouration is obtained in Lassaigne's test.
5. Reactions involving migration of an atom or a group from one atom to another within the same molecule are called ..... reactions.
6. Chemical species bearing a negative charge on carbon and possessing eight electrons in its valence shell are called .....
7. $(C_6H_5)_3C^+$ is ..... stable than $(CH_3)_3C^+$.
8. IUPAC name of $CH_2 = C(CH_3) - CHOH - CH_2CHO$ is .....
9. According to IUPAC nomenclature, alkyl cyanides are named as .....
10. Camphor, naphthalene, etc are purified by ..... method.

C. Choose the correct alternative

1. Beilstein test is used for detection of *halogens / nitrogen*.
2. The IUPAC name of is *3-Methyl pentanenitrile / 2-Methylbutanenitrile*.
3. Pent-1-ene and pent-2-ene are *position / skeleton* isomers.
4. $AlCl_3$ behaves as *electrophile / nucleophile*.
5. In Duma's method for the estimation of nitrogen, the gas collected in nitrometer is NH_3 / N_2.
6. The boiling point of glycerol is 563K but it decomposes below 563K, therefore, it is purified by *steam distillation / vacuum distillation*.
7. Homolytic fission of a covalent bond leads to the formation of *free radicals / carbanions*.
8. The hybridisation state of carbon in $C_6H_5\overset{+}{C}H_2$ carbocation is sp^2 / sp^3.
9. The number of structural isomers for hexane is *five / four*.
10. The Vital force theory about organic compounds was proposed by *Berzelius / Wohler*.

Answers QUICK MEMORY TEST

A. Say True or False

1. **False :** Hexane has 5 structural isomers.
2. **False :** Central C is *sp* hybridised while the terminal C atoms are sp^2 hybridised.
3. Fase
4. True
5. True
6. True
7. **False :** Functional isomer of methyl methanoate is ethanoic acid.
8. True
9. False
10. True

B. Complete the missing links

1. Functional
2. increases
3. trans but-2-ene
4. blood red
5. rearrangement
6. carbanions
7. more
8. 3-Hydroxy-4-methylpent-4-en-1-al
9. alkanenitriles
10. sublimation

C. Choose the correct alternative

1. Halogens
2. 3-Methylpentanenitrile
3. position
4. electrophile
5. N_2
6. vacuum distillation
7. free radicals
8. sp^2
9. five
10. Berzelius.

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HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q. 1. Why is it necessary to use acetic acid and not hydrochloric acid for acidification of sodium extract for testing sulphur by lead acetate test ?

Ans. For testing sulphur, the sodium extract is acidified with acetic acid because lead acetate is soluble and does not interefere with the test. However, if HCl is used, lead acetate will react with it forming white precipitate of lead chloride and therefore, it will interfere with the test.

$$(CH_3COO)_2Pb + 2HCl \longrightarrow 2CH_3COOH + PbCl_2$$

Lead acetate — White ppt.

Q.2. What is the cause of geometrical isomerism in alkenes ?

Ans. Alkenes have a double bond (π bond) in their molecules and there is a restricted rotation around π-bond which gives rise to geometrical isomerism.

Q. 3. Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate ? Give reason for your answer.

Ans. The precipitate of AgCl will not be formed because CCl_4 is covalent compound and does not ionise to give Cl^- ions to react with $AgNO_3$.

$$CCl_4 + AgNO_3 \longrightarrow \text{No reaction.}$$

Q. 4. Lassaigne's test is not shown by diazonium salts, though they contain nitrogen. Why ?

Ans. Diazonium salts ($C_6H_5N_2^+X^-$) readily lose N_2 on heating before reacting with fused sodium metal. Therefore, these do not give positive Lassaigne's test for nitrogen.

Q. 5. A mixture contains benzoic acid and nitrobenzene. How can this mixture be separated into its constituents by the technique of extraction using an appropriate chemical reagent ?

Ans. The mixture is shaken with sodium bicarbonate and extracted with ether or chloroform when nitrobenzene goes into organic layer. Nitrobenzene is then obtained by distillation of the solvent. The filtrate is acidified with dil. HCl and the solution is cooled. Filtration gives benzoic acid.

Q. 6. A mixture contains two components A and B. The solubilities of A and B in water near its boiling point are 30 g per 100 mL and 10 g per 100 mL respectively. How will you separate A and B from this mixture ?

Ans. It can be separated by fractional crystallization. When the saturated solution of the mixture is allowed to cool, the less soluble component (*i.e.*,B) crystallizes at first leaving the more soluble component (A) in the mixture.

Q.7. Why is an organic compound fused with sodium for testing halogens, nitrogen, sulphur and phosphorus ?

Ans. The organic compound is fused with sodium metal to convert N, S, P and halogens present in the organic compound to their corresponding sodium salts.

Q.8.Explain why the name butanol is not specific whereas the name butanone represents a specific compound.

Ans. Butanol may have —OH group on the first or the second carbon atom as

$CH_3CH_2CH_2CH_2OH$ or $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{CH}}CH_3$

Butan-1-ol — Butan-2-ol

Therefore, butanol does not represent a specific compound.

Butanone cannot have the carbonyl group at any other position :

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$$

Therefore, it represents a specific compound.

Q.9. Which continuous chain hydrocarbon is isomeric with 2-methyl-3-ethyl hexane ?

Ans. Nonane.

Q.10. Arrange the following in order of increasing stability :

$CH_3CH_2^-$, $CH{\equiv}C^-$, $CH_2{=}CH^-$

Ans. In acetylide ion, $CH{\equiv}C^-$, the carbon atom carrying the negative charge is *sp*-hybridised and has 50%, *s*-character; in $CH_2{=}CH^-$ ion, the carbon atom carrying the negative charge is sp^2-hybridised and has 33.3% *s*-character whereas in $CH_3CH_2^-$ ion, the carbon atom bearing the negative charge is sp^3 hybridised and has 25% *s*-character.

Since the *s*-electrons, on an average are closer to the nucleus than *p*-electrons, therefore, a carbon atom with larger *s*-character can accommodate or stabilize the negative charge better than a carbon atom with smaller *s*-character. In other words, the stability of carbanion increases as the *s*-character of the carbon atom carrying the negative charge increases. Now, the *s*-character of the carbon atom decreases as we move from *sp* to sp^2 to sp^3, therefore, the relative stability of the three carbanions follows the order :

$$HC{\equiv}C^- > CH_2{=}CH^- > CH_3CH_2^-$$

Q.11. Why is the carbocation F_3C^+ more stable than carbocation $F_3C{-}C\overset{+}{<}$ Explain.

Ans. In $F_3C{-}C\overset{+}{<}$, the strongly withdrawing $F_3C{-}$ group withdraws electrons of the C—C bond towards itself. As a result, the positive charge on C gets intensified and therefore, $F_3C{-}C\overset{+}{<}$ is less stable. On the other hand, in

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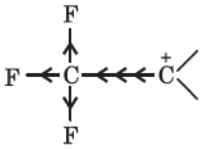
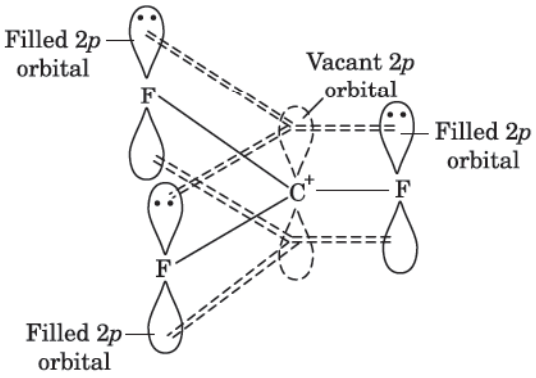
carbocation F_3C^+— lone pair of electrons on each of the three F-atoms overlaps with the empty *p*-orbital of the carbon atom carying the positive charge thereby dispersing the positive charge and thus stabilizing the carbocation F_3C^+ relative to $F_3C—C^+$



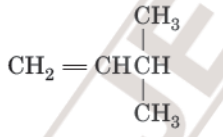
–I-effect of the F atoms destabilizes the carbocation by intensifying the +ve charge.



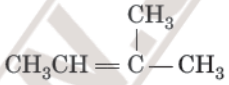
Back bonding from 2*p* orbitals of F to empty 2*p* orbital of C disperses + ve charge

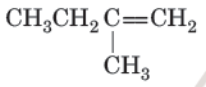
Q.12. Write structural formulae for all the compounds having molecular formula C_5H_{10}.

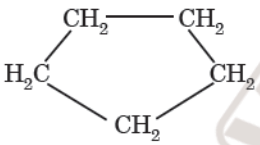
Ans. $CH_2=CHCH_2CH_2CH_3$

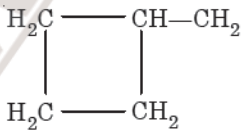


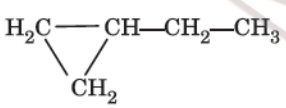
$CH_3CH=CHCH_2CH_3$

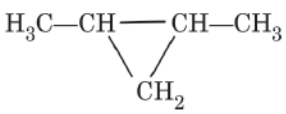


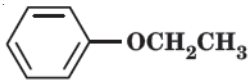




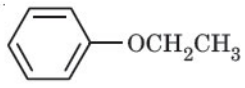






Q.13. Write metamers of 

Ans. The various metamers are I and II, I and III, I and IV, and I and V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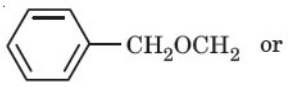
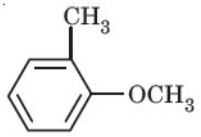

II

or


III

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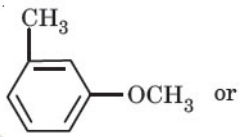
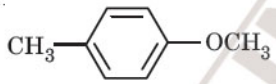

IV

or


V

Q.14. Choose electrophiles and nucleophiles from the following :

$AlCl_3$, CH_3O^-, $H_3CC{\equiv}CH$, H^-, $CH_3CH^+CH_3$, NH_3, H^-

Ans. Nucleophiles : CH_3O^-, $H_3CC{\equiv}CH$, H^-, NH_3

Electrophiles : $AlCl_3$, $CH_3CH^+CH_3$

Q.15. Draw geometrical isomers of the following :

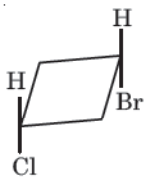
(*a*) 1-bromo-3-chlorocyclobutane

(*b*) 3, 4-dimethylhept-3-ene

(*c*) 1, 3-dibromocyclobutane

(*d*) 1, 4-dimethylcyclohexane

Ans. (*a*)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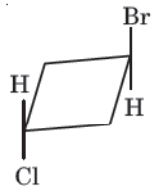
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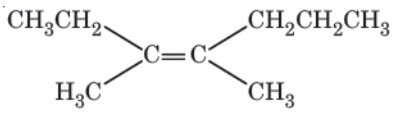
(*b*)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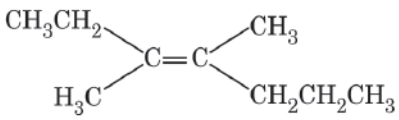
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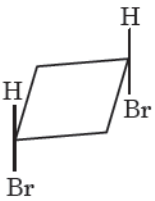
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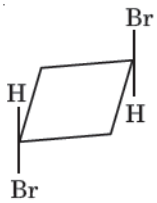
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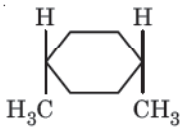
(*d*)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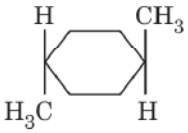
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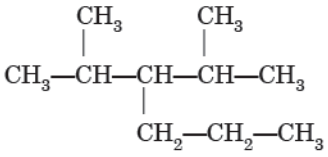
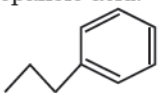
Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. What is self linking property of carbon known as ? Define it.
2. Define a functional group. Give functional groups for
   (*i*) aldehydes
   (*ii*) carboxylic acid families.
3. What is meant by tetravalency of carbon ?
4. Write the structural formula of 1,5-hexadiene.
5. Give the IUPAC name of the compound :



6. Write the correct name of an organic compound whose incorrect name is 2-ethyl- 2-pentene.
7. What are primary and secondary suffixes ?
8. Define homologous series.
9. Write the IUPAC name of freon.
10. What is dry ice ? Give its one use.
11. Name the carbide of silicon which is very hard.
12. How many secondary hydrogens are present in (*i*) isopentane and (*ii*) neo-pentane ?
13. Write the IUPAC name of isobutylene.
14. Write the formula of acetophenone.
15. An alkane has two possible names; 2, 3, 5-trimethyl hexane and 2, 4, 5-trimethyl hexane. Which of these is correct ?
16. Define inductive effect.
17. What are elimination reactions ? Give one example.
18. Define electromeric effect.
19. What are carbocations ? Arrange primary, secondary and tertiary carbocation in the order of their stability.
20. What are carbenes ? Give one example.
21. What are rearrangement reactions ? Give one example.
22. Give one example of a positional isomerism.
23. What species are formed when a covalent bond gets fissioned ?
24. Name two functional groups containing C = O group.
25. Define hyperconjugation.
26. What are electrophiles and nucleophiles ?
27. What are carbanions ? Give one example.
28. Give the examples of substitution reactions.
29. What is meant by +I and –I inductive effect ?
30. Who developed the concept of hyperconjugation ? Define.
31. Write resonating structures of CH_3COO^- ion.
32. Identify the functional groups in the following :

33. Which of the two : But-3-yn-1-ol or But-4-ol-1-yne represents correct IUPAC name ?
34. Which of the $O_2N\ CH_2\ CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why ?
35. Write bond line structural formula for 2-(4-Isobutyl phenyl) propanoic acid.
36. Give IUPAC name of 
37. Select electrophiles from the following :
    NO_2^+, $C_2H_5O^-$, Cl^+, BF_3, HS^-
38. Why is $(CH_3)_3C^+$ more stable than $CH_3CH_2^+$?
39. Write structural formula for 2-Phenyl propanal.
40. Which of the two : trans-but-2-ene-or trans- pent-2-ene is non polar ?
41. What is sublimation ?
42. What is fractional distillation ?
43. Name two methods for the estimation of nitrogen in an organic compound.
44. How will you separate ether from water ?
45. Will you get any precipitate if you add silver nitrate solution to chloromethane ? If not, why ?
46. What is the principle of chromatography ?
47. Why is Lassaigne's extract boiled with conc. HNO_3 before testing for halogens ?
48. How will you separate a mixture of naphthalene and sand ?
49. How is nitrogen detected in an organic compound ?
50. What is the formula of prussian blue ?
51. What colour will you get in Lassaigne's test if the compound contains both N and S ?
52. How will you separate two miscible liquids which differ in their boiling points by 10°C ?
53. Why is it necessary to boil the Lassaigne's extract with conc. HNO_3 before testing for halogens?
54. Give the principle of steam distillation.
55. What is the formula of iron (III) hexacyanoferrate (II) ?
56. Will CCl_4 give white precipitate of AgCl on heating with silver nitrate ? Give reason for your answer.

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57. Why an organic compound vaporizes at a temperature below its boiling point in steam distillation ?

58. Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound ?

Short Answer Questions *carrying 2 or 3 marks*

1. What is homologous series ? Write its important characteristics.

2. What is catenation ? Explain as to why carbon has maximum tendency for catenation ?

3. Write the structural formula of *n*-butane and iso-butane. Write the different types of alkyl radicals formed from these.

4. Name the different types of hydrocarbons. Give structures of two members of each type.

5. How will you decide whether the two given compounds are the homologous of the same family or not ?

6. What are isomers ? Give one example.

7. What does IUPAC name stand for ? Give three compounds with no difference in IUPAC and common names.

8. What family is represented by the general formula C_nH_{2n-2} ? Write the IUPAC and common names of the first three members of this family.

9. What are inductive and electromeric effect ? How do these two effects differ ?

10. What is hyperconjugation ? What are its important consequences ?

11. What are structural isomers ? Explain different types of structural isomers with examples.

12. Explain the following reactions with one example each.
(*i*) Elimination reaction
(*ii*) Substitution reaction

13. What are carbocations and carbanions? Explain the stability of primary, secondary and tertiary carbocations and carbanions.

14. What is hyperconjugation ? How will you explain stability of methylated alkenes on the basis of hyperconjugation ?

15. What are free radicals ? Explain its structure and stability of different types of alkyl free radicles.

16. What are reaction intermediates ? Explain with examples.

17. Explain the following types of structural isomers with one example each.
(*i*) Functional isomers (*ii*) Metamers
(*iii*) Position isomers.

18. What is tautomerism ? How does it differ from resonance ?

19. Write short note on structure and stability of carbocations.

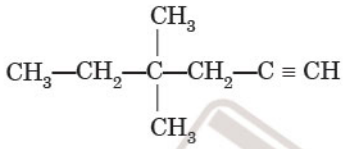
20. What is resonance ? Explain with two examples.

21. What is inductive effect ? What is meant by +I and –I effect ?

22. What are addition and rearrangement reactions ? Explain with examples.

23. (*a*) Write out the error and write the correct IUPAC names of :
(*i*) 1, 6-Hexadiene (*ii*) 2-Ethyl-2-pentene.
(*b*) Write the structural formulae of :
(*i*) 2, 3-dimethylbutane
(*ii*) 4-Methylpentyne.

24. Write IUPAC names of the following :

(*i*) 

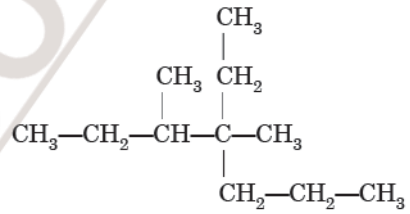
(*ii*) $CH_3—C \equiv C—C \equiv C—CH_3$

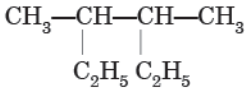
(*iii*) $CH_3—C \equiv C—CH_2—CH_3$

(*iv*) $(CH_3)_2CH—CH_2—CH = CH_2$

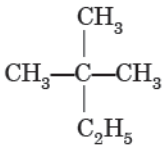
25. Write the structural formula of :
(*i*) 2, 3-dimethylbutane
(*ii*) 2-Methylpentane
(*iii*) 2, 2,4-trimethylpentane.

26. Name the following compounds according to IUPAC system :

(*i*) 

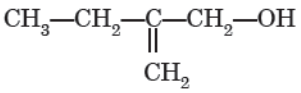
(*ii*) 

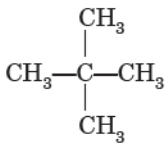
(*iii*) $(CH_3)_3C—CH_3$

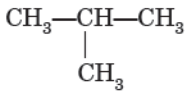
(*iv*) 

27. Give the IUPAC names of the following compounds :

(*i*) $CH_2 = CH—CH_2—CH_2—OH$

(*ii*) 

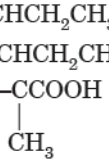
(*iii*) 

(*iv*) 

28. Write the IUPAC names of the following compounds:

(*i*) $(CH_3)_2CHCH_2CH_3$

(*ii*) $(C_2H_5)_2CHCH_2CH_3$

(*iii*) 

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29. The common names of some compounds are given below. Write their structural formula and IUPAC names :
(*i*) Neo-pentane (*ii*) Crotonaldehyde
(*iii*) Acetaldehyde (*iv*) Neo-pentyl alcohol
(*v*) Iso-butyl alcohol.

30. What are electrophiles and nucleophiles ? Give examples.

31. What is the structure of carbanion ? How is it formed ? Explain the stability of CH_3^-, 1°, 2°, 3°.

32. Draw the formulae for the first three members of each homologous series starting with
(*i*) HCOOH (*ii*) CH_3COCH_3

33. Write stick, condensation and bond line structural formulae for all the isomers of the molecular formulae.
(*i*) C_3H_{10} (*ii*) $C_3H_6O_2$ (*iii*) C_3H_8O

34. Explain why alkyl group act as electron donors when attached to a π-system.

35. What are reactive intermediates ? How are they generated by bond fission ?

36. What are electrophiles and nucleophiles ? Explain with two examples of each.

37. Describe the chemistry of Duma's method for the estimation of nitrogen.

38. Name the methods to purify impure sample of (*i*) glycerol (*ii*) benzene.

39. What is the principle of vacuum distillation ? Discuss this method.

40. Describe the principle and details of the process of steam distillation.

41. How are carbon and hydrogen detected in an organic compound ?

42. What is separating funnel ? How does it help in separating a mixture of kerosene, oil and water ?

43. Discuss the chemistry of Lassaigne's test.

44. Explain the principle of paper chromatography.

45. Describe the method, which can be used to separate two components with different solubilities in a solvent X.

46. Describe Carius method for the estimation of halogens.

47. Explain one method each for the (*i*) detection and (*ii*) estimation of sulphur in a compound.

48. Describe the chemistry of the Lassaigne's test for the detection of nitrogen.

49. What is the difference between distillation and fractional distillation ?

50. Discuss the principle and chemical reactions of Kjeldahl's method.

51. How will you estimate bromine in an organic compound ?

52. Explain the principle of Duma's method for estimation of nitrogen in a compound.

53. Discuss the principle of distillation, vacuum distillation and steam distillation.

54. How is chromatography used for the purification of organic compounds ?

55. How is sulphur detected and estimated in an organic compound ?

56. A mixture contains benzoic acid and nitrobenzene. How can this be separated into its constituents by the technique of extraction using an appropriate chemical reagent ?

57. Suggest a suitable technique of separating naphthalene from kerosene present in a mixture.

58. What is the difference between distillation, distillation under reduced pressure and steam distillation ?

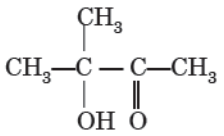
59. Differentiate between the principle for estimation of nitrogen in an organic compound by
(*i*) Dumas method (*ii*) Kjeldahl's method

60. Discuss the principle of estimation of halogen, sulphur and phosphorus present in an organic compound.

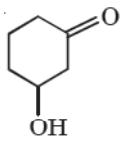
Long Answer Questions *carrying 5 marks*

1. Discuss IUPAC general rules for naming branched chain hydrocarbon.

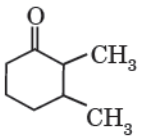
2. Write the IUPAC names of the following :
(*i*)



(*ii*)



(*iii*)



3. What is resonance ? Draw the resonating structures for the following molecules showing the electron shift using curved-arrow notation :
(*i*) $CH_2 = CHOCH_3$ (*ii*) $C_6H_5CH_2^+$
(*iii*) $C_6H_5NO_2$ (*iv*) C_6H_5OH
(*v*) $CH_3CH = CHCHO$ (*vi*) $CH_3CH = CHCH_3^+$

4. What are structural isomers ? Explain different types of structural isomers with examples.

5. What are different types of reaction intermediates formed by homolytic and heterolytic fission of a covalent bond ? Explain with examples.

6. Write short notes on
(*i*) Electromeric effect (*ii*) Inductive effect
(*iii*) Hyperconjugation

7. How are attacking reagents classified ? Explain with examples.

8. Discuss four types of organic reactions.

9. Give condensed and bond line structural formulae and identify the functional group or groups present if any :
(*a*) Hexanedial

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(*b*) 2- Hydroxy - 1,2,3- propanetricarboxylic acid

(*c*) 2-Hydroxy-1,2-diphenylethan-1-one

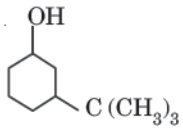
(*d*) Cycloocta-1,5-diene

(*e*) 2-(4-Isobutyl phenyl) propanoic acid.

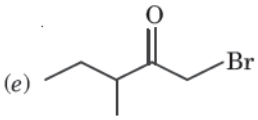
10. Write IUPAC names for the following :

(*a*) $HC \equiv C\ CH = CH\ CH = CH_2$

(*b*) $CH_3\ CO\ CH_2CH_2CH_2COOH$

(*c*) 

(*d*) $(CH_3)_2\ CHCH\ (CH_3)_2$

(*e*) 

11. Draw resonance structures for the following compounds. Show the electro shift using curved arow notation :

(*i*) C_6H_5OH (*ii*) $C_6H_5NO_2$

(*iii*) $C_6H_5CH_2^+$ (*iv*) $CH_3CH = CHCHO$

(*v*) $CH_3CH = CH\ CH_2^+$ (*vi*) C_6H_5CHO

(*vii*) $CH_2 = CHO\ CH_3$

12. Draw formulae for the first five members of each homologous series begining with the following compounds.

(*i*) $H - COOH$ (*ii*) CH_3COCH_3

(*iii*) $H - CH = CH_2$,

13. Explain with an example the following terms :

(*i*) crystallisation (*ii*) simple distillation (*iii*) steam distillation (*iv*) extraction with a solvent (*v*) fractional distillation.

14. Write the chemical equations involved in the detection of nitrogen, sulphur, halogens and phosphorus present in an organic compound.

15. Discuss Kjeldahl's method for the estimation of nitrogen in a compound.

16. How will you detect the presence of sulphur in a compound ? Discuss the method for its estimation.

17. Explain the following :

(*i*) Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens ?

(*ii*) Why is an organic compound fused with sodium for testing nitrogen, sulphur and phosphorus ?

(*iii*) Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test ?

(*iv*) CCl_4 does not give test with silver nitrate solution.

Competition File

Objective Questions

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Organic Compounds

A1. An electrophilic reagent is :

(*a*) Electron deficient species

(*b*) Electron rich species

(*c*) Negatively charged species

(*d*) A Lewis base.

A2. Which of the following carbocation will be the most stable ?

(*a*) $(CH_3)_2\ CH^+$

(*b*) $Ph_3\ C^+$

(*c*) $CH_2 = CHCH_2^+$

(*d*) $CH_3CH_2^+$

A3. The shape of carbocation is :

(*a*) Planar (*b*) Linear

(*c*) Pyramidal (*d*) Tetrahedral

A4. The structural formula for 2-ethylprop-2-en-1-ol is :

(*a*) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}} = CHOH$

(*b*) $C_2H_5CH = CHCH_2OH$

(*c*) $CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{C}} = CHCH_2OH$

(*d*) $CH_2 = \underset{\displaystyle C_2H_5}{\underset{|}{C}}HCHOH$

A5. Which of the following compound contains amide functional group ?

(*a*) $CH_3CH_2NHCH_3$

(*b*) $CH_3CH_2 - \underset{\displaystyle O}{\underset{\|}{C}} - NH_2$

(*c*) $CH_3\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH$

(*d*) $CH_3N(CH_3)_2$

Answers

A1. (*a*) **A2.** (*b*) **A3.** (*a*) **A4.** (*d*) **A5.** (*b*)

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A6. The molecule in which the distance between the neighbouring carbon atoms is least is:

(*a*) C_6H_6 (*b*) C_2H_2

(*c*) C_2H_4 (*d*) C_2H_6

A7. The hybrid orbitals that will form the compound $CH_3—C \equiv C—CH_2—CH_3$ are :

(*a*) sp^3, sp (*b*) sp, sp^2

(*c*) sp^3, sp^2 (*d*) sp, sp.

A8. The IUPAC name for the structural formula:

$$CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—CH_3$$

(*a*) 3, 4-dimethylhexane

(*b*) 2, 3-diethylbutane

(c) 2-ethyl-3-methylpentane

(*d*) Heptane.

A9. Among the following, the one having longest chain is :

(*a*) neopentane (*b*) isopentane

(*c*) 2-methylpentane (*d*) 2, 2-dimethylbutane

A10. The IUPAC name of compound having formula $(CH_3)_3C—CH = CH_2$ is :

(*a*) 3, 3, 3-trimethyl-1-propene

(*b*) 1, 1, 1-trimethyl-3-propene

(*c*) 3, 3-dimethyl-1-butene

(*d*) 1, 1-dimethyl-3-butene.

A11. The general formula of cycloalkanes is :

(*a*) C_nH_{2n} (*b*) C_nH_{2n-1}

(*c*) C_nH_{2n+1} (*d*) $C_{n+1}H_{n+2}$

A12. The IUPAC name of the compound

$CH_3—CH = CH—C \equiv CH$ is

(*a*) Pent-2-en-4-yne

(*b*) Pent-1-en-4-yne

(*c*) Pent-3-en-1-yne

(*d*) Pent-2-en-5-yne

A13. The IUPAC name of the compound

$$CH_3—\underset{\displaystyle CH(CH_3)_2}{\underset{|}{CH}}—CH_3 \text{ is}$$

(*a*) 2-isopropylpropane

(*b*) isobutane

(*c*) 2, 3-dimethyl butane

(*d*) 2, 3-dimethylhexane.

A14. Which of the following is not a cyclic compound ?

(*a*) Anthracene (*b*) Pyrole

(*c*) Phenol (*d*) Neopentane

A15. Which of the following compound does not have only one type of hybrid carbon atoms?

(*a*) $HC \equiv C - C \equiv CH$

(*b*) $CH_3—CH_2—CH_2—CH_3$

(*c*) $CH_3—C \equiv C—CH_3$

(*d*) $CH_2 = CH—CH = CH_2$

A16. Which of the following hybridization has maximum *s*-character ?

(*a*) sp

(*b*) sp^2

(*c*) sp^3

(*d*) All have same *s*-character

A17. The IUPAC name of the compound :

$$CH_3—\underset{\displaystyle O}{\underset{\|}{C}}—CH_2—CH_2OH \text{ is}$$

(*a*) 3-oxobutan-1-ol

(*b*) 1-Hydroxybutan-3-one

(*c*) 4-Hydroxybutan-2-one

(*d*) 2-oxobutan-4-ol

A18. During the reaction :

$$CH_3CONH_2 \xrightarrow{P_2O_5} CH_3CN$$

the hybridisation state of carbon changes from

(*a*) sp^3 to sp (*b*) sp^3 to sp^2

(*c*) sp^2 to sp^3 (*d*) sp^2 to sp

A19. Which of the following is not an isomer of but-1-yne ?

(*a*) But-2-yne

(*b*) But-2-ene

(*c*) Buta-1, 3- diene

(*d*) Methyl cyclopropene

A20. How many σ and π bonds are there in the molecule of tetracyanoethene ?

$(NC)_2C = C(CN)_2$

(*a*) 9σ, 7π (*b*) 5σ, 9π

(*c*) 5σ, 8π (*d*) 9σ, 9π

A21. Which out of the following series contains only nucleophiles ?

(*a*) H_2O, SO_3, H_3O^+

(*b*) $NH_3, H_2O, R–O–H$

(*c*) $NH_3, H_2O, AlCl_3$

(*d*) CN^-, SO_3, OH^-

A22. Which of the following species has electron releasing (or +I inductive) effect ?

(*a*) $–NO_2$ (*b*) –COOH

(*c*) $(CH_3)_2CH^-$ (*d*) $C_6H_5^-$

A23. Which of the following is not an electrophile ?

(*a*) Carbocation (*b*) SO_3

(*c*) Carbene (*d*) Thioalcohol

A24. Which of the following is an electrophile ?

(*a*) CN^- (*b*) ROH

(*c*) $AlCl_3$ (*d*) NH_3

Answers

A6. (*b*) **A7.** (*a*) **A8.** (*a*) **A9.** (*c*) **A10.** (*c*) **A11.** (*a*) **A12.** (*c*) **A13.** (*c*) **A14.** (*d*) **A15.** (*c*)
A16. (*a*) **A17.** (*c*) **A18.** (*d*) **A19.** (*b*) **A20.** (*d*) **A21.** (*b*) **A22.** (*c*) **A23.** (*d*) **A24.** (*c*)

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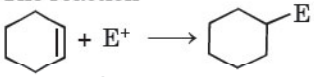
A25. Which of the following is an example of elimination reaction ?
(*a*) Chlorination of methane
(*b*) Dehydration of alcohol
(*c*) Nitration of benzene
(*d*) Hydroxylation of ethylene

A26. In which of the following, all are nucleophiles ?
(*a*) $H_2O, NO_2^+, (CH_3)_3N$
(*b*) $HS^-, BF_3, CH_3C^+=O$
(*c*) $SH^-, C_2H_5O^-, (CH_3)_3N$
(*d*) NO_2^+, BF_3, Cl^+

A27. The reaction



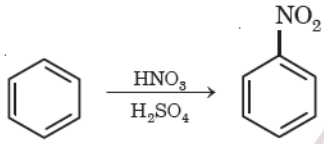
represents
(*a*) nucleophilic substitution
(*b*) electrophilic addition
(*c*) electrophilic substitution
(*d*) elimination reaction

A28. Which of the following reaction represents α, γ elimination reaction ?

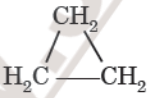
(*a*) $CH_3CHO \xrightarrow{OH^-} CH_3\overset{OH}{\overset{|}{C}}HCH_2CHO$

(*b*) $CH_3CH_2CH_2CH_2Br \xrightarrow{\text{alc. KOH}} CH_3CH_2CH=CH_2$

(*c*)



(*d*) $BrH_2C-CH_2-CH_2Br \xrightarrow{Zn\ dust}$



A29. The IUPAC name of the compound
$CH_2=CH-CH(CH_3)_2$ is
(*a*) 1,1-dimethylprop-2-ene
(*b*) 3-methylbut-1-ene
(*c*) 2-vinyl propane
(*d*) 1-isopropylethene

A30. The IUPAC name for :

is
(*a*) 1,1-dimethylbutane-1,3-diol
(*b*) 4-methylpentane-2, 4-diol
(*c*) 2-methylpentane-2, 4-diol
(*d*) 1, 3, 3- trimethylpropane-1, 3-diol

A31. The structure of 4-methylpent-2-en-1-ol is
(*a*) $CH_3CH_2CH=CHCH_2OH$
(*b*) $(CH_3)_2C=CHCH_2CH_2OH$
(*c*) $(CH_3)_2CHCH=CHCH_2OH$
(*d*) $CH_3CHOH-CH=C(CH_3)_2$

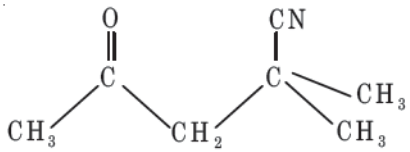
A32. The arrangement of
$(CH_3)_3C-$, $(CH_3)_2CH-$, CH_3CH_2-
when attached to benzene or unsaturated group in increasing order of inductive effect is
(*a*) $(CH_3)_3C- < (CH_3)_2CH- < CH_3CH_2-$
(*b*) $CH_3CH_2- < (CH_3)_2CH- < (CH_3)_3C-$
(*c*) $(CH_3)_2CH- < (CH_3)_3C- < CH_3CH_2-$
(*d*) $(CH_3)_3C- < CH_3CH_2- < (CH_3)_2CH-$

A33. In the compound
$CH_2=CH-CH_2-CH_2-C\equiv CH$, the C_2-C_3 bond is of the type
(*a*) $sp-sp^2$ (*b*) sp^3-sp^3
(*c*) $sp-sp^3$ (*d*) sp^2-sp^3

A34. The compounds $CH_3OC_3H_7$ and $C_2H_5OC_2H_5$ exhibit
(*a*) optical isomerism (*b*) *cis-trans* isomerism
(*c*) metamerism (*d*) chain isomerism

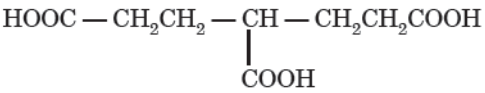
A35. The IUPAC name of $CH_3C\equiv CCH(CH_3)_2$ is
(*a*) 4-Methylpent-2-yne
(*b*) 4, 4-Dimethylbut -2-yne
(*c*) Methyl isopropylacetylene
(*d*) 2-Methylpent-4-yne

A36. The IUPAC name of the compound



is
(*a*) 4-Cyano-4-methyloxopentane
(*b*) 4-Cyano-4-methylpentan-2-one
(*c*) 2, 2-Dimethyl-4-oxopentanenitrile
(*d*) 2-Cyano-2-methyl-4-oxopentane

A37. The compound



has IUPAC name as :
(*a*) 4-carboxyheptanedioic acid
(*b*) 1,3,5-heptanetrioic acid
(*c*) Pentane-1, 3, 5-tricarboxylic acid
(*d*) 3-Carboxy heptanedioic acid

Answers

A25. (*b*) **A26.** (*c*) **A27.** (*b*) **A28.** (*d*) **A29.** (*b*) **A30.** (*c*) **A31.** (*c*) **A32.** (*a*) **A33.** (*d*) **A34.** (*c*) **A35.** (*a*) **A36.** (*c*) **A37.** (*c*)

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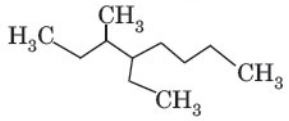
A38. Name of the compound given below is



(*a*) 4-Ethyl-3-methyloctane
(*b*) 3-Methyl-4-ethyl octane
(*c*) 2-3-Diethylheptane
(*d*) 5-Ethyl-6- methyloctane

A39. The name of some compounds are given. Which one is not in IUPAC system ?

(*a*) $CH_3CH_2CH_2\underset{\displaystyle CH_3-CH_2}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_3$
3-Methyl-4-ethylheptane

(*b*) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$
3-Methylbutan-2-ol

(*c*) $CH_3-CH_2-\underset{\displaystyle CH_2CH_3}{\underset{||}{C}}-CH-CH_3$
2-Ethyl-3-methylbut-1-ene

(*d*) $CH_3-C\equiv C-CH(CH_3)_2$
4-Methylpent-2-yne

A40. Orbital interaction between sigma bonds of a substituent group and the neighbouring pi-orbital is known as
(*a*) hyperconjugation
(*b*) inductive effect
(*c*) steric effect
(*d*) dipole-dipole interactions

Purification Techniques

A41. The principle involved in paper chromatography is
(*a*) Adsorption (*b*) Partition
(*c*) Solubility (*d*) Volatility

A42. The boiling point of glycerol is 563 K but it decomposes below 563 K. It is purified by
(*a*) sublimation (*b*) vacuum distillation
(*c*) steam distillation (*d*) fractional distillation.

A43. A mixture of acetone and methanol can be separated by
(*a*) steam distillation (*b*) vacuum distillation
(*c*) fractional distillation
(*d*) sublimation.

A44. Aniline is purified by
(*a*) Extraction with solvent
(*b*) Steam distillation
(*c*) Vacuum distillation
(*d*) Sublimation.

Qualitative Analysis of Organic Compounds

A45. In Lassaigne's test, when both N and S are present blood red colour is obtained. This is due to the formation of
(*a*) ferric ferrocyanide (*b*) ferric cyanide
(*c*) ferric thiocyanate (*d*) ferric hydroxide.

A46. Lassaigne's solution gives violet colouration with sodium nitroprusside. It indicates the presence of
(*a*) nitrogen (*b*) sulphur
(*c*) halogen (*d*) both N and S.

A47. The formula of the compound which gives violet colour in Lassaigne's test for sulphur with sodium nitroprusside is
(*a*) $Na_4[Fe(CN)_5NOS]$
(*b*) $Na_3[Fe(CN)_5NOS]$
(*c*) $Na_2[Fe(CN)_5S]$
(*d*) $Na_4[Fe(CN)_4S]$.

A48. Sodalime test for detection of N cannot be used for
(*a*) acetamide (*b*) urea
(*c*) diazo compounds (*d*) thiourea.

A49. For which of the following compound, the Lassaigne's test for N will fail ?
(*a*) $NH_2CONHNH_2HCl$
(*b*) $NH_2NH_2.2HCl$
(*c*) NH_2CONH_2
(*d*) $C_6H_5N=N-C_6H_5$

Quantitative Analysis of Organic Compounds

A50. Percentage of Se in peroxidase anhydrous enzyme is 0.5% by weight (at.wt. = 78.4), then minimum molecular weight of peroxidase anhydrous enzyme is
(*a*) 1.568×10^4 (*b*) 1.501×10^3
(*c*) 15.68 (*d*) 2.136×10^3

A51. In the Duma's method for the estimation of nitrogen, the gas collected in nitrometer is :
(*a*) N_2 (*b*) NH_3
(*c*) $N_2 + CO_2$ (*d*) CO_2.

A52. 0.4 gm of an organic compound gave 0.188 g of silver bromide by a halogen estimation method. The percentage of bromine in the compound is (at mass of Ag = 108, Br = 80)
(*a*) 39.8% (*b*) 46.0%
(*c*) 20.0% (*d*) 40.0%.

Answers

A38. (*a*) **A39.** (*a*) **A40.** (*a*) **A41.** (*b*) **A42.** (*b*) **A43.** (*c*) **A44.** (*b*) **A45.** (*c*) **A46.** (*b*) **A47.** (*a*)
A48. (*c*) **A49.** (*b*) **A50.** (*a*) **A51.** (*a*) **A52.** (*c*)

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A53. In the Duma's method for the estimation of nitrogen, 0.84 g of an organic compound gave 448 ml of nitrogen at S.T.P. The percentage of nitrogen in the compound is
(a) 33.3% (b) 66.7%
(c) 50.0% (d) 60%.

A54. In the Kjeldahl's method, the nitrogen in the organic compound is converted to
(a) Ammonium sulphate (b) Ammonia
(c) Nitric acid (d) Nitrogen.

A55. 0.395 g of an organic compound by Carius method for the estimation of S gave 0.582 g of $BaSO_4$. The percentage of S in the compound is
(a) 20.24% (b) 35.62%
(c) 12.24% (d) 40.65%.

A56. During the estimation of nitrogen by Kjeldahl's method, copper sulphate is added to
(a) raise boiling point of H_2SO_4
(b) absorb water formed
(c) catalyse the reaction
(d) form ammonium sulphate

A57. An organic compound containing C, H and N give the following on analysis :
C = 40%, H = 13.33% and N = 46.67%. What would be its empirical formula ?
(a) C_2H_7N (b) $C_2H_7N_2$
(c) CH_4N (d) CH_3N

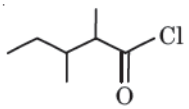
Answers

A53. (b) **A54.** (a) **A55.** (a) **A56.** (c) **A57.** (c)

B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

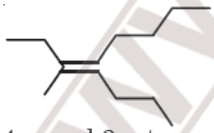
AIPMT & Other State Boards' Medical Entrance

B1. The IUPAC name of



(a) 1-chloro-1-oxo-2,3-dimethylpentane
(b) 2-ethyl-3-methylbutanoyl chloride
(c) 2,3-dimethyl pentanoyl chloride
(d) 3,4-dimethyl pentanoyl chloride
(C.B.S.E.P.M.T. 2006)

B2. Give the IUPAC name of the alkene



(a) Z-3-methyl-4-propyl-3-octene
(b) E-3-methyl-4-propyl-3-octene
(c) E-4-butyl-3-methyl-3-heptene
(d) E-2-ethyl-3-propyl-2-heptene
(e) Z-2-ethyl-3-propyl-2-heptene *(Kerala-PMT 2008)*

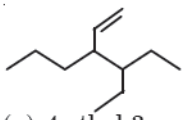
B3. Which of the following compounds will not give Lassaigne's test for nitrogen?
(a) NH_2NH_2 (b) $C_6H_5NHNH_2$
(c) PhN = NPh (d) NH_2CONH_2
(DUMET 2010)

B4. Which of the following ions is the most resonance stabilized?
(a) ethoxide (b) phenoxide
(c) *tertiary*-butoxide (d) *iso*-propoxide
(e) *n*-butoxide *(Kerala PMT 2010)*

B5. Homolytic fission of a covalent bond leads to the formation of
(a) electrophile (b) nucleophile
(c) free radical (d) carbocation
(e) carbanion *(Kerala PMT 2010)*

B6. Glycerine is purified by
(a) vacuum distillation (b) simple distillation
(c) steam distillation (d) sublimation
(e) solvent extraction *(Kerala PMT 2010)*

B7. The correct IUPAC name for the compound



is
(a) 4-ethyl-3-propylhex-1-ene
(b) 3-ethyl-4-ethenylheptane
(c) 3-ethyl-4-propylhex-5-ene
(d) 3-(1-ethylpropyl) hex-1-ene *(AIPMT 2011)*

B8. In Dumas' method of estimation of nitrogen 0.35 g of an organic compound gave 55 mL of nitrogen collected at 300 K temperature and 715 mm pressure. The percentage composition of nitrogen in the compound would be (aqueous tension at 300 K = 15 mm).
(a) 15.45 (b) 16.45
(c) 17.45 (d) 14.45 *(AIPMT 2011)*

B9. The Lassaigne's extract is boiled with conc. HNO_3 while testing for halogens. By doing so it
(a) decomposes Na_2S and NaCN, if formed
(b) helps in the precipitation of AgCl
(c) increases the solubility product of AgCl
(d) increases the concentration of NO_3^- ions
(AIPMT 2011)

Answers

B1. (c) **B2.** (a) **B3.** (a) **B4.** (b) **B5.** (c) **B6.** (a) **B7.** (a) **B8.** (b) **B9.** (a)

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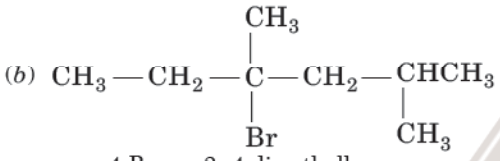
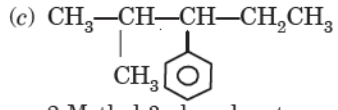
B10. Aniline is separated from aniline-water mixture by
(*a*) crystallization (*b*) steam distillation
(*c*) solvent extraction (*d*) sublimation
(*e*) differential extraction (*Kerala P.M.T. 2012*)

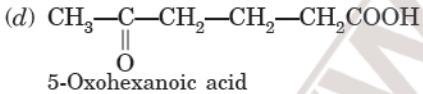
B11. Only *sp* and sp^2 hybrid orbitals are involved in the formation of
(*a*) $CH_3—CH = CH_2$ (*b*) $CH_3—CH_3$
(*c*) $CH_3—C\equiv CH$ (*d*) $CH_2=C=CH_2$
(*e*) $CH_3—C\equiv C—CH_3$ (*Kerala P.M.T. 2012*)

B12. A sample of 0.5 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5M H_2SO_4. The remaining acid after neutralisation by ammonia consumed 80 mL of 0.5 M NaOH. The percentage of nitrogen in the organic compound is
(*a*) 14 (*b*) 28
(*c*) 42 (*d*) 56
(*e*) 70 (*Kerala P.M.T. 2012*)

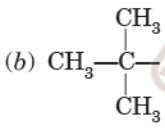
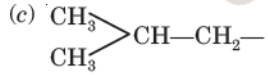
B13. Which nomenclature is not according to IUPAC system?
(*a*) $Br—CH_2—CH=CH_2$
1-Bromoprop-2-ene

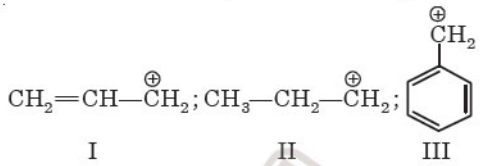
(*b*) 
4-Bromo-2, 4-dimethylhexane

(*c*) 
2-Methyl-3-phenylpentane

(*d*) 
5-Oxohexanoic acid

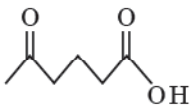
(*A.I.P.M.T. 2012*)

B14. The structure of isobutyl group in an organic compound is
(*a*) $CH_3—CH_2—CH_2—CH_2—$
(*b*) 
(*c*) 
(*d*)
(*NEET 2013*)

B15. The order of stability of the following carbocations is

I II III
(*a*) III > I > II (*b*) III > II > I
(*c*) II > III > I (*d*) I > II > III
(*NEET 2013*)

B16. In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10 mL of 1 M H_2SO_4. The percentage of nitrogen in the soil is
(*a*) 37.33 (*b*) 45.33
(*c*) 35.33 (*d*) 43.33 (*AIPMT 2014*)

B17. Which of the following organic compound has same hybridization as its combustion product (CO_2) ?
(*a*) Ethane (*b*) Ethyne
(*c*) Ethene (*d*) Ethanol
(*AIPMT 2014*)

B18. What is the IUPAC name of the following compound?

(*a*) Hexa-2,6-dienone-6-ol
(*b*) 2-Ketohexanoic acid (*c*) 5-Ketohexanoic acid
(*d*) 2-Oxohexanoic acid (*e*) 5-Oxohexanoic acid
(*Kerala PMT 2015*)

B19. The number of σ and π-bonds present in 1, 3-butadiene are respectively
(*a*) 9 and 2 (*b*) 8 and 2
(*c*) 9 and 3 (*d*) 9 and 1
(*e*) 8 and 1 (*Kerala PMT 2015*)

B20. Which of the following statement is not correct for a nucleophile?
(*a*) Nucleophiles attack low electron density sites
(*b*) Nucleophiles are not electron seeking
(*c*) Nucleophile is a Lewis acid
(*d*) Ammonia is a nucleophile (*AIPMT 2015*)

B21. Two possible stereo-structures of $CH_3CHOH.COOH$, which are optically active, are called:
(*a*) Enantiomers (*b*) Mesomers
(*c*) Diastereomers (*d*) Atropisomers
(*AIPMT 2015*)

Answers

B10. (*b*) **B11.** (*d*) **B12.** (*b*) **B13.** (*a*) **B14.** (*c*) **B15.** (*a*) **B16.** (*a*) **B17.** (*b*) **B18.** (*e*) **B19.** (*a*) **B20.** (*c*) **B21.** (*a*)

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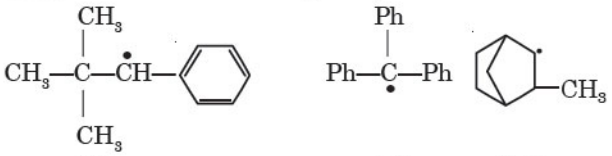
B22. Consider the following compounds:



(I) (II) (III)

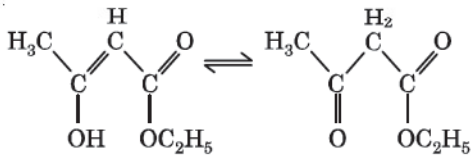
Hyperconjugation occurs in

(a) III only (b) I and III

(c) I only (d) II only

(AIPMT 2015)

B23. The enolic form of ethyl acetoacetate as shown below has



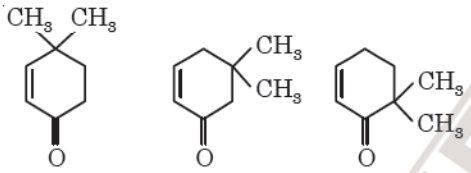
(a) 9 sigma bonds and 2 pi–bonds

(b) 9 sigma bonds and 1 pi–bond

(c) 18 sigma bonds and 2 pi–bonds

(d) 16 sigma bonds and 1 pi–bond. *(AIPMT 2015)*

B24. Given:



(I) (II) (III)

Which of the given compounds can exhibit tautomerism?

(a) II and III (b) I, II and III

(c) I and II (d) I and III

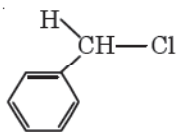
(AIPMT 2015)

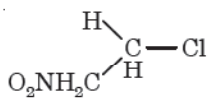
B25. In Duma's method for estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at 300 K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is

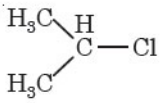
(a) 16.76 (b) 15.76

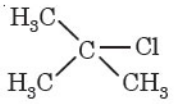
(c) 17.36 (d) 18.20 *(AIPMT 2015)*

B26. In which of the following compounds, the C—Cl bond ionisation shall give most stable carbonium ion?

(a) 

(b) 

(c) 

(d) 

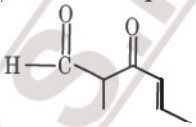
(AIPMT 2015)

B27. The pair of electrons in the given carbanion, $CH_3C{\equiv}C^-$, is present in which of the following orbitals?

(a) sp^2 (b) sp

(c) $2p$ (d) sp^3 *(NEET 2016)*

B28. The IUPAC name of compound



is _____.

(a) 5-formylhex-2-en-3-one

(b) 5-methyl-4-oxohex-2-en-5-al

(c) 3-keto-2-methylhex-5-enal

(d) 3-keto-2-methylhex-4-enal *(NEET 2017)*

B29. The correct statement regarding electrophile is

(a) electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile

(b) electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile

(c) electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile

(d) electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile. *(NEET 2017)*

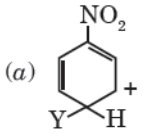
B30. Which of the following is correct with respect to –I effect of the substituents? (R = alkyl)

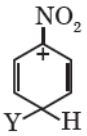
(a) $-NH_2 < -OR < -F$ (b) $-NR_2 < -OR < -F$

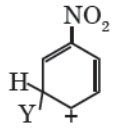
(c) $-NH_2 > -OR > -F$ (d) $-NR_2 > -OR > -F$

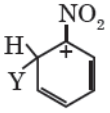
(NEET 2018)

B31. Which of the following carbocation is expected to be most stable ?

(a) 

(b) 

(c) 

(d) 

(NEET 2018)

Answers

B22. (a) **B23.** (c) **B24.** (b) **B25.** (a) **B26.** (d) **B27.** (d) **B28.** (d) **B29.** (c) **B30.** (a) **B31.** (c)

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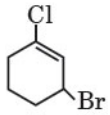
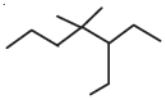
B32. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is
(*a*) *n*-hexane (*b*) 2,3-Dimethylbutane
(*c*) 2,2-Dimethylbutane
(*d*) 2-Methylpentane *(A.I.E.E.E. 2005)*

B33. The IUPAC name of the compound

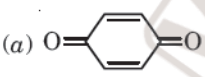
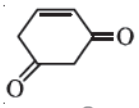
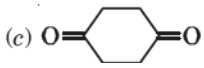
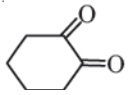


is
(*a*) 6-bromo-2-chlorocyclohexene
(*b*) 3-bromo-1-chlorocyclohexene
(*c*) 1-bromo-3-chlorocyclohexene
(*d*) 2-bromo-6-chlorocyclohex-1-ene
(A.I.E.E.E. 2006)

B34. The increasing order of stability of the following free radicals is
(*a*) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
(*b*) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
(*c*) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C}H < (C_6H_5)_2\dot{C}H$
(*d*) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$
(A.I.E.E.E. 2006)

B35. The IUPAC name of  is
(*a*) 4,4-Dimethyl-5,5-diethyl pentane
(*b*) 5,5-Diethyl-4,4-dimethyl pentane
(*c*) 3-ethyl-4,4,-dimethyl heptane
(*d*) 1,1-diethyl-2,2-dimethyl pentane
(A.I.E.E.E. 2007)

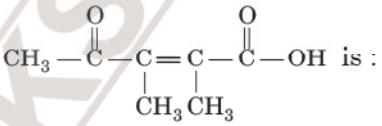
B36. Which one of the following carbanions is least stable?
(*a*) $CH_3CH_2^-$ (*b*) $HC{\equiv}C^-$
(*c*) $(C_6H_5)_3C^-$ (*d*) CH_3^-
(*e*) $(CH_3)_3C^-$ *(Kerala PET. 2008)*

B37. Which of the following does not exhibit tautomerism?
(*a*) 
(*b*) 
(*c*) 
(*d*) 
(WB-JEE 2008)

B38. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is
(*a*) $-CONH_2$, $-CHO$, $-SO_3H$, $-COOH$
(*b*) $-COOH$, $-SO_3H$, $-CONH_2$, $-CHO$
(*c*) $-SO_3H$, $-COOH$, $-CONH_2$, $-CHO$
(*d*) $-CHO$, $-COOH$, $-SO_3H$, $-CONH_2$ *(AIEEE 2008)*

B39. Methoxy methane and ethanol are
(*a*) Functional isomers (*b*) Optical isomers
(*c*) Position isomers (*d*) Chain isomers
(AIEEE 2008)

B40. The IUPAC name of the molecule

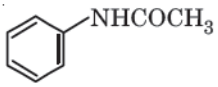
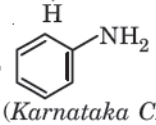


is :
(*a*) 4-Oxo-2, 3-dimethylpent-2-en-1-oic acid
(*b*) 2-Carboxy-3-methylpent-2-en-3-one
(*c*) 4-Carboxy-3-methylpent-3-en-2-one
(*d*) 2,3-Dimethyl-4-oxo-pent-2-en-1-oic acid
(J & K CET 2009)

B41. 0.25 g of an organic compound on Kjeldahl's analysis gave enough ammonia to just neutralise 10 cm^3 of 0.5 M H_2SO_4. The percentage of nitrogen in the compound is
(*a*) 28 (*b*) 56 (*c*) 14 (*d*) 112
(*e*) 42 *(Kerala Engg. 2009)*

B42. The number of isomers including stereoisomers possible for the compound having molecular formula C_4H_8 is
(*a*) one (*b*) two (*c*) three (*d*) four
(J.K. CET 2010)

B43. In Kjeldahl's method, ammonia from 5 g of food neutralizes 30 cm^3 of 0.1 N acid. The percentage of nitrogen in the food is
(*a*) 0.84 (*b*) 8.4 (*c*) 16.8 (*d*) 1.68
(Karnataka CET 2010)

B44. Which one of the following has the most nucleophilic nitrogen?
(*a*)
(*b*)
(*c*) 
(*d*) 
(Karnataka CET 2010)

B45. In Lassaigne's test for the detection of halogens, the sodium fusion extract is first boiled with concentrated nitric acid. This is
(*a*) to remove silver halides
(*b*) to decompose Na_2S and NaCN, if present
(*c*) to dissolve Ag_2S
(*d*) to dissolve AgCN, if formed
(*e*) because Ag_2S and AgCN are insoluble in nitric acid
(Kerala PET 2010)

Answers

B32. (*b*) **B33.** (*b*) **B34.** (*d*) **B35.** (*c*) **B36.** (*e*) **B37.** (*a*) **B38.** (*c*) **B39.** (*a*) **B40.** (*d*) **B41.** (*a*)
B42. (*d*) **B43.** (*a*) **B44.** (*a*) **B45.** (*b*)

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B46. Hyper conjugation is most useful for stabilizing which of the following carbocations?
(*a*) *neo*-Pentyl (*b*) *tert*-Butyl (*c*) *iso*-Propyl
(*d*) Ethyl (*e*) Methyl (*Kerala PET 2010*)

B47. The IUPAC name of the following compound is

$(CH_3)_2CH-CH_2CH=CH-CH=CH-CH(C_2H_5)CH_3$

(*a*) 1, 1, 7, 7-tetramethyl-2,5-octadiene
(*b*) 2, 8-dimethyl-3,6-decadiene
(*c*) 1,5-di-*iso*-propyl-1, 4-hexadiene
(*d*) 3, 9-dimethyl-4, 6-decadiene
(*e*) 2, 8-dimethyl-4, 6-decadiene (*Kerala PET 2010*)

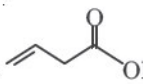
B48. 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is :
(*a*) 23.7 (*b*) 29.5 (*c*) 59.0 (*d*) 47.4
(*AIEEE 2010*)

B49. The correct order of boiling points of 2, 2-dimethylpropane, 2-methylbutane and *n*-pentane is
(*a*) *n*-pentane > 2, 2-dimethylpropane > 2-methylbutane
(*b*) *n*-pentane > 2-methylbutane > 2, 2-dimethylpropane
(*c*) 2,2-dimethylpropane > 2-methylbutane > *n*-pentane
(*d*) 2-methylbutane > *n*-pentane > 2,2-dimethylpropane
(*e*) 2-methylbutane > 2,2-dimethylpropane > *n*-pentane (*Kerala PET 2011*)

B50. The stablest radical among the following is
(*a*) $C_6H_5CH_2-\dot{C}H_2$ (*b*) $CH_3\dot{C}H_2$
(*c*) $C_6H_5-\dot{C}H-CH_3$ (*d*) $CH_3-\dot{C}H-CH_3$
(*e*) $CH_3-CH_2-\dot{C}H_2$ (*Kerala PET 2011*)

B51. The compounds $CH_3CH=CHCH_3$ and $CH_3CH_2CH=CH_2$
(*a*) are tautomers (*b*) are position isomers
(*c*) contain same number of sp^3 - sp^3, sp^3 - sp^2 and sp^2 – sp^2 carbon-carbon bonds
(*d*) exist together in dynamic equilibrium
(*e*) are optical isomers (*Kerala PET 2011*)

B52. In hexa-1,3-diene-5-yne, the number of C—C σ, C—C π and C—H σ bonds respectively are
(*a*) 5, 4 and 6 (*b*) 6, 3 and 5
(*c*) 5, 3 and 6 (*d*) 6, 4 and 5
(*e*) 5, 5 and 5 (*Kerala PET 2011*)

B53. The IUPAC name of  is
(*a*) but-3-enoic acid (*b*) but-1-enoic acid
(*c*) pent-4-enoic acid (*d*) prop-2-enoic acid
(*Karnataka PET 2011*)

B54. 1.2 g of an organic compound on Kjeldahlization liberates ammonia which consumes 30 cm^3 of 1 N HCl. The percentage of nitrogen in the organic compound is
(*a*) 30 (*b*) 35
(*c*) 46.67 (*d*) 20.8
(*Karnataka PET 2011*)

B55. Identify the compound that exhibits tautomerism.
(*a*) 2-Butene (*b*) Lactic acid
(*c*) 2-Pentanone (*d*) Phenol (*AIEEE 2011*)

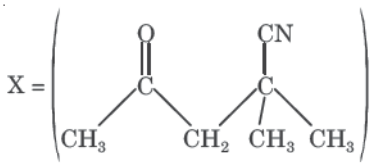
B56. Among the following carbocations :
(I) $Ph_2C^+CH_2Me$ (II) $PhCH_2CH_2CH^+Ph$
(III) Ph_2CHCH^+Me (IV) $Ph_2C(Me)CH_2^+$
the order of stability is
(*a*) IV > II > I > III (*b*) I > II > III > IV
(*c*) II > I > IV > III (*d*) I > IV > III > II
(*W.B.J.E.E. 2012*)

B57. In the estimation of sulphur by Carius method, 0.480 g of an organic compound gives 0.699 g of barium sulphate. The percentage of sulphur in this compound is
(Atomic masses : Ba = 137, S = 32, O = 16)
(*a*) 20% (*b*) 15% (*c*) 35%
(*d*) 30% (*e*) 40% (*Kerala P.E.T. 2012*)

B58. The IUPAC name of $CH_3CHOHCH_2CH(CH_3)CHO$ is
(*a*) 2-hydroxy-4 methylpentanal
(*b*) 4-hydroxy-2 methylpentanal
(*c*) 2-hydroxy-3 methylpentanal
(*d*) 2-methylpent-4-ol-1-al (*AMU Engg. 2012*)

B59. The enolic form of acetone contains
(*a*) 9 sigma bonds, 2 pi bonds and 1 lone pair
(*b*) 9 sigma bonds, 1 pi bond and 2 lone pairs
(*c*) 8 sigma bonds, 2 pi bonds and 2 lone pairs
(*d*) 10 sigma bonds, 1 pi bond and 1 lone pair
(*AMU Engg. 2012*)

B60. The IUPAC name of the compound X is

X = 

(*a*) 4-cyano-4-methyl-2-oxopentane
(*b*) 2-cyano-2-methyl-4-oxopentane
(*c*) 2, 2-dimethyl-4-oxopentanenitrile
(*d*) 4-cyano-4-methyl-2-pentanone (*W.B. JEE 2013*)

Answers

B46. (*b*) **B47.** (*e*) **B48.** (*a*) **B49.** (*b*) **B50.** (*c*) **B51.** (*b*) **B52.** (*a*) **B53.** (*a*) **B54.** (*b*) **B55.** (*c*)
B56. (*b*) **B57.** (*a*) **B58.** (*b*) **B59.** (*b*) **B60.** (*c*)

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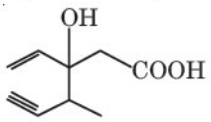
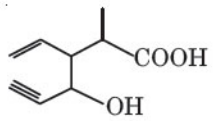
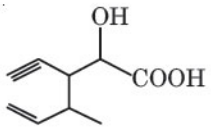
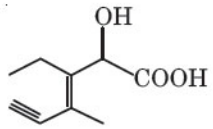
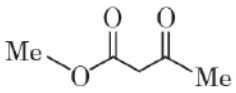
Competition File

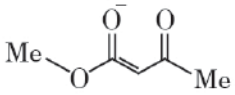
B61. Structure of the compound whose IUPAC name is 3-Ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is

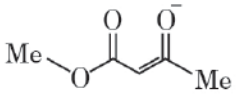
(a) 
(b) 
(c) 
(d) 

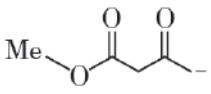
(J.K. C.E.T. 2013)

B62. Among the following structures the one which is not a resonating structure of others is


I


II


III


IV

(a) I (b) II
(c) III (d) IV *(WB JEE 2014)*

B63. On complete combustion, 0.246 g of an organic compound gave 0.198 g of CO_2 and 0.1014 g of H_2O. The ratio of carbon and hydrogen atoms in the compound is

(a) 1 : 3 (b) 1 : 2
(c) 2 : 5 (d) 2 : 7 *(A.M.U. Engg. 2014)*

B64. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the ammonia evolved was absorbed in 60 mL of M/10 sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralisation. The percentage of nitrogen in the compound is

(a) 6% (b) 10%
(c) 3% (d) 5% *(JEE Main 2014)*

B65. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (at. mass Ag = 108 ; Br = 80)

(a) 48 (b) 60
(c) 24 (d) 36 *(JEE Main 2015)*

B66. The distillation technique most suited for separating glycerol from spent lye in the soap industry is

(a) Simple distillation
(b) Fractional distillation
(c) Steam distillation
(d) Distillation under reduced pressure.

(JEE Main 2016)

B67. Identify the correct statement in the following:

(a) Dimethyl ether and ethanol are chain isomers.
(b) Ethanoic acid and methyl methanoate are position isomers.
(c) *n*-butane and isobutane are functional isomers.
(d) Propan-1-ol and propan-2-ol are position isomers.

(Karnataka CET 2017)

B68. Lassaigne's test (with silver nitrate) is commonly used to detect halogens such as chlorine, bromine and iodine but not useful to detect fluorine because the product AgF formed is

(a) volatile (b) reactive
(c) explosive (d) soluble in water
(e) a liquid *(Kerala PET 2017)*

B69. What is the IUPAC nomenclature of the given compound?

(a) 5-Ethynyl-1, 6-heptadiene
(b) 3-Ethynyl-1, 6-heptadiene
(c) 3-Vinyl-hept-6-en-1-yne
(d) 5-Vinyl-hept-1-en-6-yne *(J.K. CET 2018)*

B70. During the fusion of organic compound with sodium metal, nitrogen present in the organic compound is converted into

(a) $NaNO_2$ (b) $NaNH_2$
(c) NaCN (d) NaNC

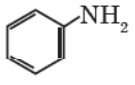
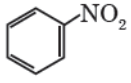
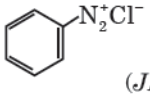
(Karnataka CET 2018)

B71. The elution sequence of a mixture of compounds containing chlorobenzene, anthracene and *p*-cresol developed on an alumina column using a solvent system of progressively increasing polarity is

(a) anthracene → chlorobenzene → *p*-cresol
(b) anthracene → *p*-cresol → chlorobenzene
(c) chlorobenzene → *p*-cresol → anthracene
(d) chlorobenzene → anthracene → *p*-cresol
(e) *p*-cresol → anthracene → chlorobenzene

(Kerala PET 2018)

B72. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation ?

(a)
(b) 
(c) 
(d) 

(JEE Main 2018)

Answers

B61. (d) **B62.** (d) **B63.** (c) **B64.** (b) **B65.** (c) **B66.** (d) **B67.** (d) **B68.** (d) **B69.** (b) **B70.** (c)
B71. (a) **B72.** (b)

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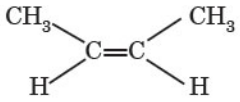
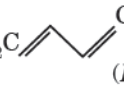
Competition File

JEE (Advance) for IIT Entrance

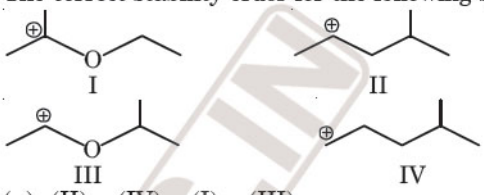
B73. Which of the following compounds will exhibit geometrical isomerism ?
(*a*) 1-Phenylbut-2-ene
(*b*) 3-Phenylbut-1-ene
(*c*) 2-Phenylbut-1-ene
(*d*) 1,1-Diphenylprop-1-ene *(I.I.T. 2000)*

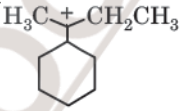
B74. Which of the following has the lowest dipole moment?
(*a*) 
(*b*) $CH_3C \equiv CCH_3$
(*c*) $CH_3CH_2C \equiv CH$
(*d*) $CH_2{=}CH{-}C{\equiv}CH$ *(I.I.T. 2002)*

B75. Which of the following represents the given mode of hybridisation sp^2—sp^2—sp—sp from left to light ?
(*a*) $H_2C{=}CH{-}C{\equiv}N$ (*b*) $HC{\equiv}C{-}C{\equiv}CH$
(*c*) $H_2C{=}C{=}C{=}CH_2$ (*d*) 
(I.I.T. 2003)

B76. The number of structural isomers for C_6H_{14} is
(*a*) 3 (*b*) 4
(*c*) 5 (*d*) 6 *(I.I.T. 2007)*

B77. Hyperconjugation involves overlap of the following orbitals
(*a*) $\sigma - \sigma$ (*b*) $\sigma - p$
(*c*) $p - p$ (*d*) $\pi - \pi$ *(IIT-JEE 2008)*

B78. The correct stability order for the following species is

(*a*) (II) > (IV) > (I) > (III)
(*b*) (I) > (II) > (III) > (IV)
(*c*) (II) > (I) > (IV) > (III)
(*d*) (I) > (III) > (II) > (IV) *(IIT-JEE 2008)*

B79. The total number of contributing structures showing hyperconjugation (involving C—H bonds) for the following carbocation is

(*a*) six (*b*) four
(*c*) eight (*d*) three *(IIT-JEE 2011)*

Answers

B73. (*a*) **B74.** (*b*) **B75.** (*a*) **B76.** (*c*) **B77.** (*b*) **B78.** (*b*) **B79.** (*a*)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. The dipole moment is shown by
(*a*) 1,4-Dichlorobenzene
(*b*) *cis*-1,2-Dichloroethene
(*c*) *trans*-1,2-Dichloroethene
(*d*) *trans*-1,2-Dichloro-1-pentene

C2. Keto-enol tautomerism is shown by
(*a*) C_6H_5CHO (*b*) $C_6H_5COCH_3$
(*c*) $C_6H_5COC_6H_5$ (*d*) $C_6H_5COCH_2COCH_3$

C3. Which of the following compounds contain only sp^3 hybridized carbon ?
(*a*) Cycloalkanes (*b*) Branched chain alkanes
(*c*) Benzene (*d*) Cycloalkenes

C4. Which of the following are not nucleophiles?
(*a*) BF_3 (*b*) $RCOO^-$
(*c*) ROR (*d*) NO_2^+

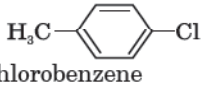
C5. The species having +I effect are
(*a*) CH_3CH_2 (*b*) —COOH
(*c*) $-NO_2$ (*d*) $(CH_3)_3C$ —

C6. The pairs having only electrophiles are :
(*a*) BF_3, CH_3^+ (*b*) $RCOO^-$, NH_3
(*c*) $AlCl_3$, SO_3 (*d*) SO_3, ROR

C7. Which of the following behave both as nucleophile as well as an electrophile ?
(*a*) CH_3Cl (*b*) HCHO
(*c*) CH_3CN (*d*) CH_3OH

C8. Which of the following compounds contain all the carbon atoms in the same hybridisation state?
(*a*) $H-C\equiv C-C\equiv C-H$
(*b*) $CH_2=CH-CH=CH_2$
(*c*) $CH_3-C\equiv C-CH_3$
(*d*) $CH_2=C=CH_2$

C9. Which of the following groups contain only electrophiles?
(*a*) BF_3, NH_3, H_2O (*b*) $AlCl_3$, SO_3, NO_2^+
(*c*) NO_2^+, CH_3^+, CH_3—C=O (*d*) $C_2H_5^-$, C_2H_5, $C_2H_5^+$

C10. The IUPAC name(s) of the following compound is(are)

(*a*) 4-methylchlorobenzene
(*b*) 4-chlorotoluene
(*c*) 1-chloro-4-methylbenzene
(*d*) 1-methyl-4-chlorobenzene *(JEE Advance 2017)*

Answers

C1. (*b, d*) **C2.** (*b, d*) **C3.** (*a, b*) **C4.** (*a, d*) **C5.** (*a, c*) **C6.** (*a, c*) **C7.** (*b, c*) **C8.** (*a, b*) **C9.** (*b, c*) **C10.** (*b, c*)

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D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

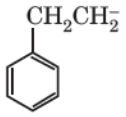
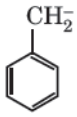
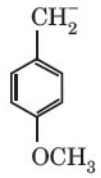
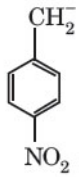
Passage

Organic compounds mainly consist of covalent bonds. The electron pair in these covalent bonds may undergo displacement either of their own or under the influence of other species. The cleavage of covalent bond between two atoms takes place in homolytic or heterolytic fashion. The homolytic fission results into free radicals while heterolytic fission results into carbocations and carbanions. These are also called reaction intermediates and are attacked by electrophiles and nucleophiles. The electrophiles seek electron rich sites while nucleophiles seek electron deficient sites.

Answer the followings Questions :

D1. Which of the following series contain only nucleophiles:
(*a*) $AlCl_3$, BF_3, NH_3 (*b*) $RCOO^-$, CH_3^-, CN^-
(*c*) NH_3, SO_3, ROR (*d*) NO_2^+, BF_3, Cl^+

D2. Which of the following is the most stable cation ?
(*a*) $F_3C—CH_2^+$ (*b*) $(CH_3)_2CH^+$
(*c*) CH_3^+ (*d*) CF_3^+ *(J & K C.E.T. 2004)*

D3. The most stable carbanion among the following is
(*a*)  (*b*) 
(*c*)  (*d*)  *(D.C.E. 2000)*

D4. The most stable free radical among the following is
(*a*) $C_6H_5CH_2\dot{C}H_2$ (*b*) $C_6H_5\dot{C}HCH_3$
(*c*) $CH_3\dot{C}H_2$ (*d*) $CH_3\dot{C}HCH_3$

D5. The most stable carbocation is:
(*a*) CH_3^+ (*b*) $(CH_3)_3C^+$
(*c*) $CH_3CH_2CH_2^+$ (*d*) $(CH_3)_2CH^+$

D6. The hybridisation state of carbon in the carbocation $C_6H_5CH_2^+$ is
(*a*) *sp* (*b*) sp^2
(*c*) sp^3 (*d*) *sp* or sp^2

D7. Which of the following is most stable carbocation ?
(*a*) Ph_2CH^+ (*b*) $PhCH_2^+$
(*c*) Ph_3C^+ (*d*) Ph^+

D8. Diazomethane decomposes in the presence of light to give
(*a*) free radical (*b*) carbocation
(*c*) carbenes (*d*) carbanion

Answers

D1. (*b*) **D2.** (*b*) **D3.** (*d*) **D4.** (*b*) **D5.** (*b*) **D6.** (*b*) **D7.** (*c*) **D8.** (*c*)

Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Ue the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
(*c*) If assertion is CORRECT, but reason is INCORRECT.
(*d*) If assertion is INCORRECT, but reason is CORRECT.
(*e*) If both assertion and reason are INCORRECT.

1. Assertion : Allyl free radical is more stable than simple free radical.
Reason : The allyl free radical is stabilized by reasonance. *(A.I.I.M.S. 2001)*

2. Assertion : In allene (C_3H_4) all carbon atoms are sp^2 hybridised.
Reason : All the three carbon atoms are joined by double bond.

3. Assertion : Lassaigne's test is not shown by diazonium salts.
Reason : Diazonium salts lose N_2 on heating much before than they have a chance to react with fused sodium.

4. Assertion : A mixture of *o*-nitrophenol and *p*-nitrophenol can be separated by steam distillation.
Reason : *p*-nitrophenol is steam volatile while *o*-nitrophenol is not steam volatile.

Answers

1. (*a*) **2.** (*d*) **3.** (*a*) **4.** (*c*)

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5. Assertion : The Lassaigne extract is boiled with dil HNO_3 before testing for halogens.
Reason : Ag_2S is soluble in HNO_3.

6. Assertion : $(CH_3)_3C^+$ is less stable than $(CH_3)_2CH_2^+$ ion.
Reason : $(CH_3)_3C^+$ has pyramidal structure.

7. Assertion : Alkanes having more than three carbon atoms exhibit chain isomerism.
Reason : All carbon atoms in alkanes are sp^3 hybridized.

8. Assertion : Dumas method is more applicable to nitrogen containing compounds than Kjeldahl's method.
Reason : Kjeldahl's method does not give satisfactory results for compounds in which nitrogen is bonded to oxygen.

9. Assertion : Butane and 2-methyl butane are homologues.
Reason : Butane is a straight chain alkane while 2-methyl butane is a branched chain alkane.

10. Assertion : Methylene has a sextet of electrons.
Reason : Methylene behaves as a nucleophile.

11. Assertion : $CH_3C^+{=}O$ behaves as electrophile.
Reason : In this species, O has two pairs of electrons.

12. Assertion : All the C—C bond lengths in benzene are equivalent.
Reason : The resonance energy of benzene is about 150.6 kJ mol^{-1}.

13. Assertion : Simple distillation can help in separating a mixture of propan-1-ol (boiling point 97° C) and propanone (boiling point 56°C).
Reason : Liquids with a difference of more than 20°C in their boiling points can be separated by simple distillation.

14. Assertion : All the carbon atoms in $H_2C{=}C{=}CH_2$ are sp^2 hybridised.
Reason : In this molecule all the carbon atoms are attached to each other by double bonds.

15. Assertion : Sulphur present in an organic compound can be estimated quantitatively by Carius method.
Reason : Sulphur is separated easily from other atoms in the molecule and gets precipitated as light yellow solid.

16. Assertion : Components of a mixture of red and blue inks can be separated by distributing the components between stationary and mobile phases in paper chromatography.
Reason : The coloured components of inks migrate at different rates because paper selectively retains different components according to the difference in their partition between the two phases.

17. Assertion : Pent-1-ene and pent-2-ene are position isomers.
Reason : Position isomers differ in the position of functional group or a substituent.

Answers

5. (c) **6.** (e) **7.** (b) **8.** (b) **9.** (b) **10.** (c) **11.** (c) **12.** (b) **13.** (a) **14.** (d) **15.** (e) **16.** (a) **17.** (a)

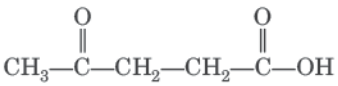
NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

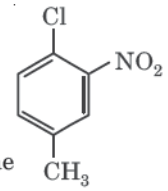
1. Which of the following is the correct IUPAC name ?
(a) 3-Ethyl-4, 4-dimethylheptane
(b) 4, 4-Dimethyl-3-ethylheptane
(c) 5-Ethyl-4, 4-dimethylheptane
(d) 4, 4-Bis(methyl)-3-ethylheptane

2. The IUPAC name for



(a) 1-hydroxypentane-1, 4-dione
(b) 1, 4-dioxopentanol
(c) 1-carboxybutan-3-one
(d) 4-oxopentanoic acid

3. The IUPAC name for



(a) 1-Chloro-2-nitro-4-methylbenzene
(b) 1-Chloro-4-methyl-2-nitrobenzene
(c) 2-Chloro-1-nitro-5-methylbenzene
(d) *m*-Nitro-*p*-chlorotoluene

Answers

1. (a) **2.** (d) **3.** (b)

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4. Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk is most electronegative ?

(*a*) $CH_3—CH_2—*CH_2—CH_3$

(*b*) $CH_3—*CH=CH—CH_3$

(*c*) $CH_3—CH_2—C\equiv *CH$

(*d*) $CH_3—CH_2—CH=*CH_2$

5. In which of the following, functional group isomerism is not possible ?

(*a*) Alcohols (*b*) Aldehydes

(*c*) Alkyl halides (*d*) Cyanides

6. The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is :

(*a*) Distillation

(*b*) Crystallisation

(*c*) Distillation under reduced pressure

(*d*) Steam distillation

7. During hearing of a court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results ?

(*a*) Column chromatography

(*b*) Solvent extraction

(*c*) Distillation

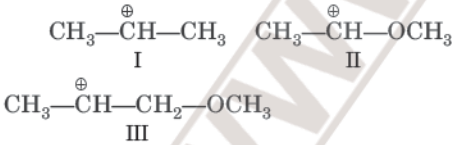
(*d*) Thin layer chromatography

8. The principle involved in paper chromatography is

(*a*) Adsorption (*b*) Partition

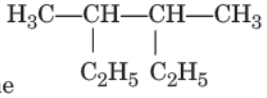
(*c*) Solubility (*d*) Volatility

9. What is the correct order of decreasing stability of the following cations :



(*a*) II > I > III (*b*) II > III > I

(*c*) III > I > II (*d*) I > II > III

10. Correct IUPAC name for  is

(*a*) 2-ethyl-3-methylpentane

(*b*) 3, 4-dimethylhexane

(*c*) 2-sec-butylbutane

(*d*) 2, 3-dimethylbutane

11. In which of the following compounds the carbon marked with asterisk is expected to have great positive charge ?

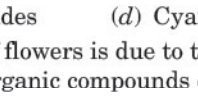
(*a*) $*CH_3—CH_2—Cl$

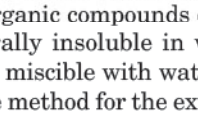
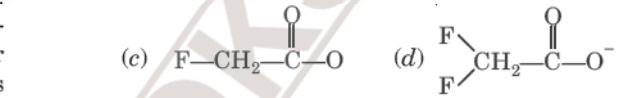
(*b*) $*CH_3—CH_2—Mg^+Cl^-$

(*c*) $*CH_3—CH_2—Br$

(*d*) $*CH_3—CH_2—CH_3$

12. Ionic species are stabilised by the dispersal of charge. Which of the following carboxylate ion is the most stable ?

(*a*)  (*b*)

(*c*)  (*d*) 

13. Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.

$H_3C—HC=CH_2 + H^+ \longrightarrow ?$

(*a*) 2° Carbanion (*b*) 1° Carbocation

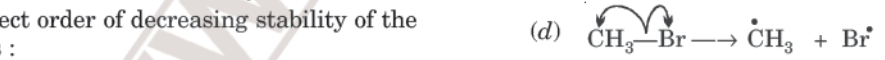
(*c*) 2° Carbocation (*d*) 1° Carbanion

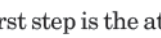
14. Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of $CH_3—Br$ is

(*a*)

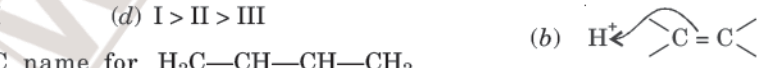
(*b*)

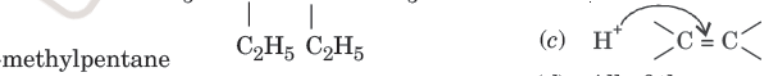
(*c*)

(*d*) 

15. The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to  portion which can be shown as

(*a*)

(*b*) 

(*c*) 

(*d*) All of these are possible

Answers

4. (*c*) **5.** (*c*) **6.** (*d*) **7.** (*d*) **8.** (*b*) **9.** (*a*) **10.** (*b*) **11.** (*a*) **12.** (*d*) **13.** (*c*) **14.** (*b*) **15.** (*b*)

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Multiple Choice Questions (Type-II)

16. Which of the following compounds contain all the carbon atoms in the same hybridisation state ?

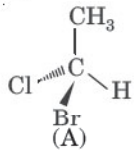
(*a*) $H-C\equiv C-C\equiv C-H$

(*b*) $CH_3-C\equiv C-CH_3$

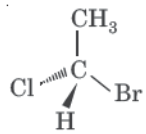
(*c*) $CH_2=C=CH_2$

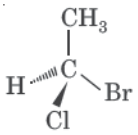
(*d*) $CH_2=CH-CH=CH_2$

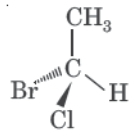
17. In which of the following representations given below spatial arrangement of group/atom different from the given in structure 'A'?

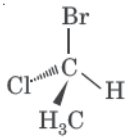


(A)

(*a*) 

(*b*) 

(*c*) 

(*d*) 

18. Electrophiles are electron seeking species. Which of the following groups contain only electrophiles ?

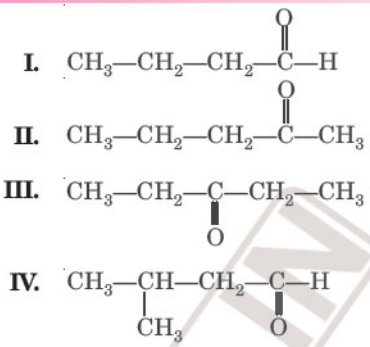
(*i*) BF_3, NH_3, H_2O

(*ii*) $AlCl_3, SO_3, NO_2^+$

(*iii*) $NO_2^+, CH_3^+, CH_3-\overset{+}{C}=O$

(*iv*) $C_2H_5^-, \dot{C}_2H_5, C_2H_5^+$

Note : Consider the following four compounds for answering questions 19 and 20.



I. $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

II. $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

III. $CH_3-CH_2-\underset{O}{\overset{\|}{C}}-CH_2-CH_3$

IV. $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H$

19. Which of the following pairs are position isomers ?

(*a*) I and II (*b*) II and III

(*c*) II and IV (*d*) III and IV

20. Which of the following pairs are **not** functional group isomers ?

(*a*) II and III (*b*) II and IV

(*c*) I and IV (*d*) I and II

21. Nucleophile is a species that should have

(*a*) a pair of electrons to donate

(*b*) positive charge

(*c*) negative charge

(*d*) electron deficient species

22. Hyperconjugation involves delocalisation of _____.

(*a*) electrons of carbon-hydrogen σ bond of an alkyl group directly attached to an atom of unsaturated system.

(*b*) electrons of carbon-hydrogen σ bond of alkyl group directly attached to the positively charged carbon atom.

(*c*) π-electrons of carbon-carbon bond

(*d*) lone pair of electrons

Answers

16. (*a, d*) **17.** (*a, c, d*) **18.** (*b, c*) **19.** (*b*) **20.** (*a, c*) **21.** (*a, c*) **22.** (*a, b*)

Matching Type Questions

In the following questions more than one correlation is possible between options of Column I and Column II. Make as many correlations as you can.

23. Match the type of mixture of compounds in Column I with the technique of separation/purification given in Column II.

Column I	*Column II*
(*i*) Two solids which have different solubitities in a solvent and which do not undergo reaction when dissolved in it.	(*a*) Steam distillation.
(*ii*) Liquid that decomposes at its boiling point.	(*b*) Fractional distillation
(*iii*) Steam volatile liquid.	(*c*) Simple distillation
(*iv*) Two liquids which have boiling points close to each other.	(*d*) Distillation under reduced pressure.
(*v*) Two liquids with large difference in boiling points.	(*e*) Crystallisation.

Answers

23. (*i*) – (*e*); (*ii*) – (*d*); (*iii*) – (*a*); (*iv*) – (*b*); (*v*) – (*c*)

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24. Match the terms mentioned in Column I with the terms in Column II.

Column I	*Column II*
(*i*) Carbocation	(*a*) Cyclohexane and 1-hexene
(*ii*) Nucleophile	(*b*) Conjugation of electrons of C—H σ bond with empty *p*-orbital present at adjacent positively charged carbon.
(*iii*) Hyperconjugation	(*c*) sp^2 hybridised carbon with empty *p*-orbital.
(*iv*) Isomers	(*d*) Ethyne
(*v*) *sp* hybridisation	(*e*) Species that can receive a pair of electrons
(*vi*) Electrophile	(*f*) Species that can supply a pair of electrons.

25. Match Column I with Column II.

Column I	*Column II*
(*i*) Dumas method	(*a*) $AgNO_3$
(*ii*) Kjeldahl's method	(*b*) Silica gel
(*iii*) Carius method	(*c*) Nitrogen gas
(*iv*) Chromatography	(*d*) Free radicals
(*v*) Homolysis	(*e*) Ammonium sulphate

26. Match the intermediates given in Column I with their probable structure in Column II.

Column I	*Column II*
(*i*) Free radical	(*a*) Trigonal planar
(*ii*) Carbocation	(*b*) Pyramidal
(*iii*) Carbanion	(*c*) Linear

27. Match the ions given in Column-I with their nature given in Column-II.

Column I	*Column II*
(*i*) $CH_3—\ddot{O}—\overset{\oplus}{C}H—CH_3$	(*a*) Stable due to resonance
(*ii*) $F_3—C^{\oplus}$	(*b*) Destabilised due to inductive effect
(*iii*) $CH_3—\underset{CH_3}{\overset{CH_3}{\underset{\vert}{\overset{\vert}{C}}}}{}^{\ominus}$	(*c*) Stabilised by hypercongugation
(*iv*) $CH_3—\overset{\oplus}{C}H—CH_3$	(*d*) A secondary carbocation

Answers

24. (*i*) – (*c*, *e*); (*ii*) – (*f*); (*iii*) – (*b*); (*iv*) – (*a*); (*v*) – (*d*); (*vi*) – (*e*) **25.** (*i*) – (*c*); (*ii*) – (*e*); (*iii*) – (*a*); (*iv*) – (*b*); (*v*) – (*d*)
26. (*i*) – (*a*); (*ii*) – (*a*); (*iii*) – (*b*) **27.** (*i*) – (*a*, *b*, *d*); (*ii*) – (*b*); (*iii*) – (*b*); (*iv*) – (*c*, *b*)

Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

(*a*) Both A and R are correct and R is the correct explaination of A.
(*b*) Both A and R are correct but R is not the correct explanation of A.
(*c*) Both A and R are not correct.
(*d*) A is not correct but R is correct.

28. Assertion (A) : Simple distillation can help in separating a mixture of propan-1-ol (boiling point 97°C) and propanone (boiling point 56°C)
Reason (R) : Liquids with a difference of more than 20°C in their boiling points can be separated by simple distillation.

29. Assertion (A) : Energy of resonance hybrid is equal to the average of energies of all canonical forms.
Reason (R) : Resonance hybrid cannot be presented by a single structure.

30. Assertion (A) : Pent-1-ene and pent-2-ene are position isomers.
Reason (R) : Position isomers differ in the position of functional group or a substituent.

31. Assertion (A) : All the carbon atoms in $H_2C=C=CH_2$ are sp^2 hybridised.
Reason (R) : In this molecule, all the carbon atoms are attached to each other by double bonds.

32. Assertion (A) : Sulphur present in an organic compound can be estimated quantitatively by Carius method.
Reason (R) : Sulphur is separated easily from other atoms in the molecule and gets precipitated as light yellow solid.

33. Assertion (A) : Components of a mixture of red and blue inks can be separated by distributing the components between stationary and mobile phases in paper chromatography.
Reason (R) : The coloured components of inks migrate at different rates because paper selectively retains different components according to the difference in their partition between the two phases.

Answers

28. (*a*) **29.** (*d*) **30.** (*a*) **31.** (*d*) **32.** (*c*) **33.** (*a*)

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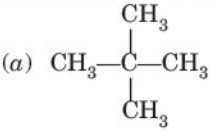
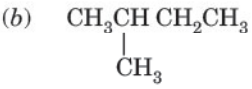
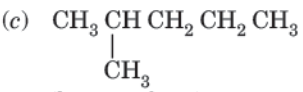
Hints & Explanations for *Difficult Objective Type Questions*

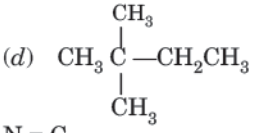
A. *mcq with only one correct answer*

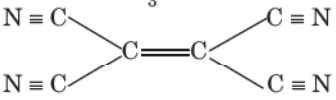
A2. (*b*) : Ph_3C^+ is most sable because of resonance stabilization among the phenyl groups.

A9. (*c*) : (*a*) 

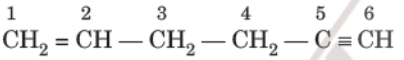
(*b*) 

(*c*) 
(longest chain)

(*d*) 

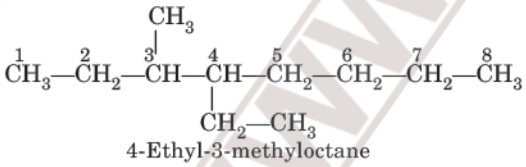
A20. (*d*) :  : 9σ and 9π

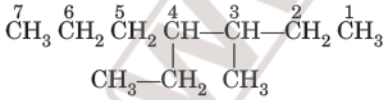
A33. (*d*) : When both double and triple bonds are present in a molecule and if there is choice, the numbering is done from the end which gives lowest number to a double bond.



C_2 — sp^2, C_3 – sp^3.

A38. (*a*) :


4-Ethyl-3-methyloctane

A39. (*a*) : 
Correct name: 4-Ethyl-3-methylheptane

A45. (*c*) : $Na + C + N + S \longrightarrow NaCNS$

$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)_3]$

Ferric thiocyanate

A50. (*a*) : Minimum molecular weight $= \dfrac{78.5\times100}{0.5}$

$= 1.568 \times 10^4$

A52. (*c*) : Mass of halogen in 0.4 g of compound

$= \dfrac{80}{188} \times 0.188$

$= 0.08$ g

$\%\ Br = \dfrac{0.08}{0.4} \times 100$

$= 20\%$

A53. (*b*) 22400 mL of nitrogen at S.T.P. weigh

$= 28$ g

448 mL of nitrogen at S.T.P. weigh

$= \dfrac{28}{22400} \times 448 = 0.56$ g

$\%$ Nitrogen $= \dfrac{0.56}{0.84} \times 100$

$= 66.7$

A55. (*a*) 233 g of $BaSO_4$ contain S = 32 g

0.582 g of $BaSO_4$ contain S $= \dfrac{32}{233} \times 0.582$

$= 0.0799$ g

$\%\ S = \dfrac{0.0799}{0.395} \times 100$

$= 20$

A57. (*c*) : $C : H : N = \dfrac{40}{12} : \dfrac{13.33}{1} : \dfrac{46.67}{14}$

$= 3.33 : 13.33 : 3.33$

$= 1 : 4 : 1$

Empirical formula CH_4N

B. *mcq from competitive examinations*

B1. (*c*) :
2,3-dimethylpentanoyl chloride

B3. (*a*) : In hydrazine, nitrogen is not directly attached to carbon. Therefore, it does not give Lassaigne's test.

B8. (*b*) : Calculating V_2 from gas equation :

$\dfrac{p_1V_1}{T_1} = \dfrac{p_2V_2}{T_2}$

or $\dfrac{700\times55}{300} = \dfrac{760\times V_2}{273}$

$V_2 = \dfrac{700\times55\times273}{300\times760}$

$= 46.098$ mL

$\%\ N = \dfrac{28}{22400} \times \dfrac{46.098}{0.35} \times 100$

$= 16.46\%$

B11. (*d*) : $\overset{sp^3}{CH_3}—\overset{sp^2}{CH}=\overset{sp^2}{CH_2}$

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$\overset{sp^3}{CH_3}—\overset{sp^3}{CH_3}$

$\overset{sp^3}{CH_3}—\overset{sp}{C}\equiv\overset{sp}{CH}$

$\overset{sp^2}{CH_2}=\overset{sp}{C}=\overset{sp^2}{CH_2}$

$\overset{sp^3}{CH_3}—\overset{sp}{C}\equiv\overset{sp}{C}—\overset{sp^3}{CH_3}$

B12. (*b*) : Unused acid required = 80 mL of 0.5 M NaOH

80 mL of 0.5 M NaOH = 40 mL of 0.5 M H_2SO_4

Volume of acid used = (50 – 40) mL of 0.5 M H_2SO_4

= 10 mL of 0.5 M H_2SO_4

% of Nitrogen = $\dfrac{1.4 \times \text{Molarity of acid} \times \text{Basicity} \times \text{Vol. of acid used}}{\text{Mass of compound taken}}$

$= \dfrac{1.4 \times 0.5 \times 2 \times 10}{0.5} = 28$

B13. (*a*) : $Br—\overset{3}{C}H_2—\overset{2}{C}H=\overset{1}{C}H_2$

3-Bromoprop-1-ene

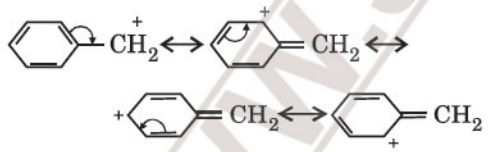
B14. (*c*) : Isobutyl group is $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—$

B15. (*a*) : I. $CH_2=CH—\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2—CH=CH_2$:

Stabilised by resonance.

II. $CH_3—CH_2—\overset{+}{C}H_2$

: Stabilised by hyperconjugation

III. 

Highly resonance stabilised

Greater the number of resonance structures greater is the stability. Hence correct order is :

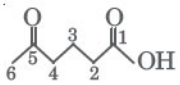
III > I > II

B16. (*a*) : According to Kjeldahl's method,

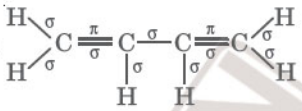
$$\%\text{ of N} = \frac{1.4 \times \text{Molarity of } H_2SO_4 \times \text{twice the Volume of } H_2SO_4 \text{ used}}{\text{Mass of substance taken}}$$

$$= \left(\frac{1.4 \times 1 \times 20}{0.75}\right) = 37.33\%$$

B17. (*b*) : The hybridisation of 'C' in CO_2 is *sp*. Therefore, the organic compound having same hybridisation as CO_2 is ethyne.

B18. (*e*) : 

5-Oxohexanoic acid

B19. (*a*) : 

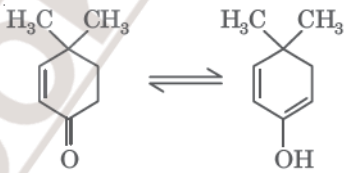
9 σ and 2π bonds:

B20. (*c*) : Nucleophile is a Lewis base.

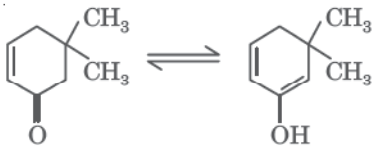
B22. (*a*) : Only structure (III) has H in conjugation with free radical. Structures I and II donot have any H in conjugation with free radical and hence donot show hyperconjugation.

B24. (*b*) : All the three

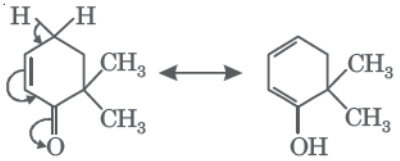
(I) In keto-enol tautomerism, α – H participates



(II) In this case, α – H participates



(III) In this case, γ – H participates



B25. (*a*) : Vapour pressure of gas = 725 – 25 = 700 mm Hg

To calculate volume at S.T.P.

V_1 = 40 mL $\quad V_2$ = ?

P_1 = 700 mm $\quad P_2$ = 760 mm

T_1 = 300 K $\quad T_2$ = 273 K

Applying $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

or $V_2 = \dfrac{P_1V_1T_2}{P_2T_1} = \dfrac{700 \times 40 \times 273}{760 \times 300}$

= 33.53 mL

22400 mL of N_2 at S.T.P. weigh = 28 g

33.53 mL of N_2 at S.T.P. weigh $= \dfrac{28}{22400} \times 33.53$

= 0.0419 g

% of nitrogen $= \dfrac{0.0419}{0.25} \times 100$

= 16.76%

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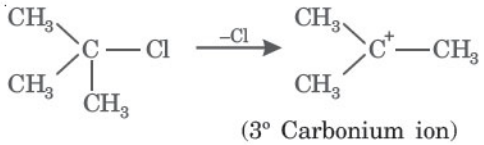
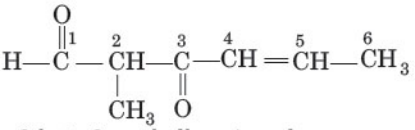
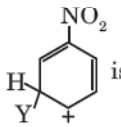
B26. (*d*) 

(3° Carbonium ion)

B28. (*d*) : 

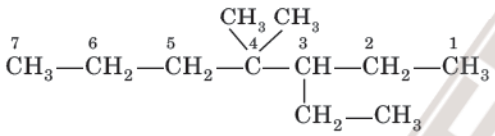
3-keto-2-methylhex-4-enal

B31. (*c*) : $-NO_2$ group is meta-directing group and will stabilize an electrophile at *m*-position. Therefore,

 is most stable

B32. (*b*) : $CH_3-CH(CH_3)-CH(CH_3)-CH_3$ will give

$ClCH_2-CH(CH_3)-CH(CH_3)-CH_3$ and $CH_3-C(Cl)(CH_3)-CH(CH_3)-CH_3$

B35. (*c*) : 

3-Ethyl-4,4-dimethyl heptane

B36. (*e*) : More are the alkyl groups, lesser is the stability of carbanions.

B37. (*a*) : This is because (*a*) is extra stable due to presence of conjugated double bond system.

B41. (*a*) : 0.5 M of 10 cm^3 H_2SO_4 ≡ 0.5 M 20 cm^3 of NH_3

1000 cm^3 of 1 M ammonia contain = 14 g of nitrogen

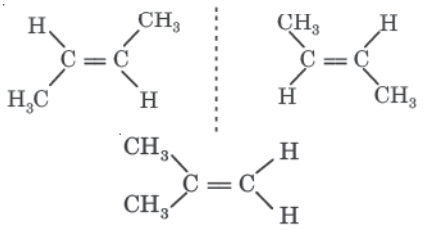
20 cm^3 of 0.5 M ammonia contain

$= \frac{14}{1000} \times 20 \times 0.5$ g nitrogen = 0.14 g

Percentage of N = $\frac{0.14}{0.5} \times 100 = 28\%$

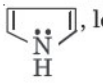
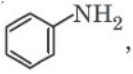
B42. (*d*) :

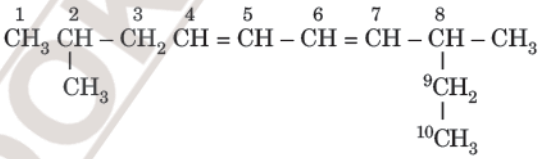
trans-but-2-ene *cis*-but-2-ene



B43. (*a*) : Percentage of nitrogen $= \frac{1.4 \times N_1 \times V}{w}$

$= \frac{1.4 \times 0.1 \times 30}{5} = 0.84\%$

B44. (*a*) : In  , lone pair of nitrogen is taking part in aromaticity. In , nitrogen is attached to electron withdrawing group. In  , lone pair of nitrogen is in resonance with benzene ring. Therefore, all these are less nucleophilic.

B47. (*e*) : 

2, 8-Dimethyl-4, 6-decadiene

B48. (*a*) :

$M_1V_1 = M_2V_2$

(HCl) (NaOH)

$0.1 \times V = 0.1 \times 15$

$V_{HCl} = 15$ ml

∴ Volume of HCl used by NH_3

$= 20 - 15 = 5$ ml

$\%$ of N $= \frac{1.4\,NV}{W}$

N = Normality of acid used

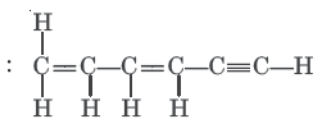
V = Volume of acid used

W = wt. of organic compound

For HCl, normality = Molarity (∵ Basicity is 1)

$\%$ of N $= \frac{1.4 \times 0.1 \times 5}{29.5 \times 10^{-3}} = 23.73\%$

B49. (*b*) : The boiling points of branched chain alkanes are less than the straight chain isomers.

B52. (*a*) : 

C—C σ bonds = 5

C—C π bonds = 4

C—H σ bonds = 6

B54. (*b*) : % N =

$1.4 \times \frac{\text{Normality of acid} \times \text{Vol. used with } NH_3}{\text{Wt. of organic compound}}$

$= \frac{1.4 \times 1 \times 30}{1.2} = 35$

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B57. (*a*) : Percentage of S =

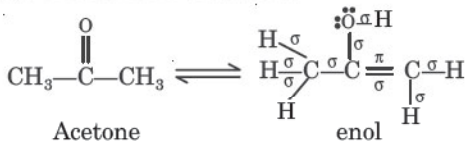
$$\frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

$$= \frac{32}{233} \times \frac{0.699}{0.480} \times 100 = 20\%$$

B58. (*b*) : $\overset{5}{C}H_3\overset{4}{C}H(OH)\overset{3}{C}H_2\overset{2}{C}H(CH_3)\overset{1}{C}HO$

4-Hydroxy-2-methylpentanal

B59. (*b*) : Enolic form of acetone



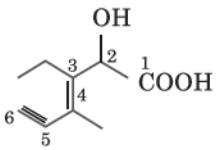
Acetone enol

9 σ bonds, 1 π bond and 2 lone pairs.

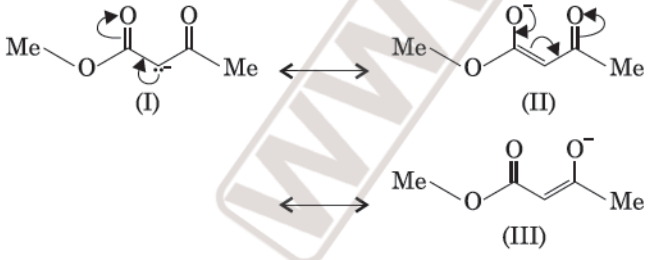
B60. (*c*) : $\overset{5}{C}H_3-\overset{4}{C}(=O)-\overset{3}{C}H_2-\overset{2}{C}(CN)(CH_3)-\overset{1}{C}H_3$

2, 2-Dimethyl-4-oxopentane nitrile

B61. (*d*) : $\overset{6}{H}C\equiv\overset{5}{C}-\overset{4}{C}(CH_3)=\overset{3}{C}(CH_2CH_3)-\overset{2}{C}H(OH)-\overset{1}{C}OOH$



B62. (*d*): I, II and III are resonating structures of each other.



B63. (*c*): % of C $= \frac{12}{44} \times \frac{\text{Mass of } CO_2}{\text{Mass of compound}} \times 100$

$$= \frac{12}{44} \times \frac{0.198}{0.246} \times 100 = 21.95\%$$

% of H $= \frac{2}{18} \times \frac{\text{Mass of } H_2O}{\text{Mass of compound}} \times 100$

$$= \frac{2}{18} \times \frac{0.1014}{0.246} \times 100 = 4.58\%$$

Element	Percentage	At. mass	Relative no. of atoms	Simple ratio
C	21.95	12	$\frac{21.95}{12} = 1.83$	1 or 2
H	4.58	1	$\frac{4.58}{1} = 4.58$	2.5 or 5

B64: (*b*): Volume of $\frac{M}{10}$ H_2SO_4 taken = 60 mL

20 mL of $\frac{M}{10}$ NaOH = $\frac{20}{2}$ mL of $\frac{M}{10}$ H_2SO_4

$\therefore$ Volume of $\frac{M}{10}$ H_2SO_4 used for neutralisation of ammonia = 60 – 10 = 50 mL

Now 50 mL of $\frac{M}{10}$ $H_2SO_4 \equiv 2 \times 50$ mL of $\frac{M}{10}$ NH_3

= 100 mL of $\frac{M}{10}$ NH_3

1000 mL of 1M NH_3 contain nitrogen = 14 g

100 mL of $\frac{M}{10}$ NH_3 contain nitrogen

$$= \frac{14}{1000} \times \frac{100 \times 1}{10} = 0.14 \text{ g}$$

$\therefore$ % of N $= \frac{0.14}{14} \times 100 = 10\%$

B65. (*c*) : % of Br $= \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance}} \times 100$

$$= \frac{80}{188} \times \frac{141}{250} \times 100$$

$$= 24$$

B67. (*d*) : $\underset{\text{Dimethylether}}{CH_3OCH_3}$ $\underset{\text{Ethanol}}{CH_3CH_2OH}$: Functional isomers

$\underset{\text{Ethanoic acid}}{CH_3COOH}$ $\underset{\text{Methylmethanoate}}{H-C(=O)-OCH_3}$: Functional isomers

$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3}$ $\underset{\text{Isobutane}}{CH_3-CH(CH_3)-CH_3}$: Chain isomers

$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$ $\underset{\text{Propan-2-ol}}{CH_3CH(OH)CH_3}$: Position isomers

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B68. (*d*) : AgF is soluble in water and does not form precipitate.

B69. (*b*) : $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H=\overset{7}{C}H_2$ with $\overset{3}{C}$ bearing a branch $C\equiv CH$

3-Ethynyl-1, 6-heptadiene

B72. (*b*) : Kjeldahl's method is suitable for the estimation of N in aniline. Nitrogen in the ring, $-NO_2$ group and $-Cl^-$ group fail to give this test.

B73. (*a*) : $C_6H_5C(CH_3)=CHCH_3$ shows geometrical isomerism.

B75. (*a*) : $\overset{sp^2}{H_2}C=\overset{sp^2}{C}H-\overset{sp}{C}\equiv\overset{sp}{N}$

B78. (*b*) : (I), (II), (III) and (IV) have 6, 5, 3 and 2 hyperconjugating H-atoms. More are hyperconjugating atoms, more is the stability.

NCERT Exemplar Problems: MCQs Type I

4. (*c*) : Electronegativity increases as the state of hybridisation changes from sp^3 to sp^2 to sp. Therefore, *sp*-carbon, $CH_3CH_2C\equiv CH$ is the most electronegative.

5. (*c*) : Alkyl halides donot show functional isomerism.

6. (*d*) : Extraction of oils from flowers is done with the help of steam distillation.

7. (*d*) : The constituents of ink can be identified and separated by thin layer chromatography.

8. (*b*) : Thin layer chromatography is based on the principle of partition.

9. (*a*) : $CH_3\rightarrow\overset{+}{C}H\leftarrow CH_3$ (I) Stabilized by weak +I effect of two methyl groups

$CH_3-\overset{+}{C}H-\ddot{O}-CH_3$ (II) Stabilized by strong +R effect of the $-OCH_3$ group

$CH_3-\overset{+}{C}H\rightarrow CH_2\rightarrow OCH_3$ (III) Destabilized by –I effect of $-OCH_3$ group

Thus, the correct order of stability of carbocation decreases as II > I > III

10. (*b*) : $CH_3-\overset{4}{C}H(-{}^5CH_2-{}^6CH_3)-\overset{3}{C}H(-{}^2CH_2-{}^1CH_3)-CH_3$ 3,4-Dimethylhexane

11. (*a*) : CH_3-CH_2-Cl

$^*CH_3-CH_2-Mg^+Cl^-$

$^*CH_3-CH_2-Br$

$^*CH_3-CH_2-CH_3$

Since Cl has highest electronegativity, structure (*a*) will have highest positive charge on C*.

12. (*d*) : Maximum dispersal of charge because of two F atoms.

13. (*c*) : Secondary (2°) carbocation is formed as the intermediate

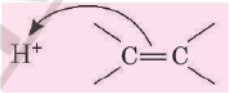
$H_3C-\overset{\curvearrowleft}{C}H=CH_2+H^+\longrightarrow CH_3-\overset{+}{C}H-CH_3$

2° Carbocation

14. (*b*) : $CH_3-Br\longrightarrow\overset{+}{C}H_3+Br^-$

Since Br is more electronegative (2.8) than carbon (2.5), therefore, heterolytic fission occurs in such a way that Br gets the –ve charge and CH_3 gets the +ve charge.

15. (*b*) : Double bond is a source of electrons and charge flows from source of more to less electron density. Therefore, π-electrons of the double bond attack the proton as



NCERT Exemplar Problems: MCQs Type II

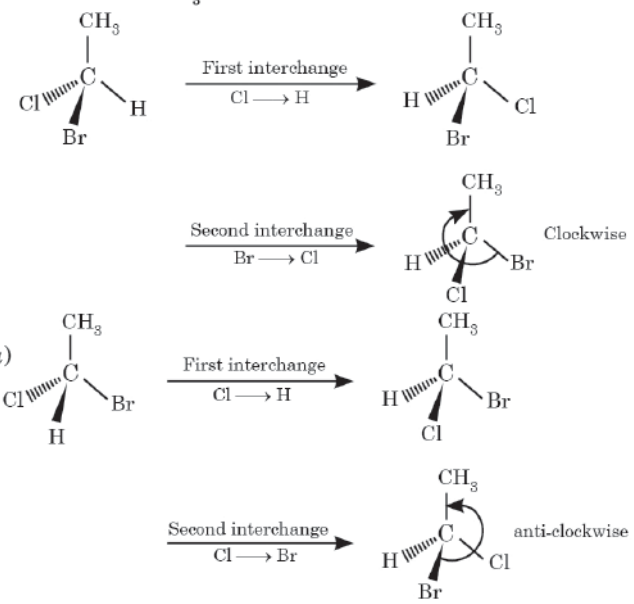
16. (*a, d*) : (*a*) $H-\overset{sp}{C}\equiv\overset{sp}{C}-\overset{sp}{C}\equiv\overset{sp}{C}-H$

(*b*) $\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv\overset{sp}{C}-\overset{sp^3}{CH_3}$

(*c*) $\overset{sp^2}{C}H_2=\overset{sp}{C}=\overset{sp^2}{C}H_2$

(*d*) $\overset{sp^2}{C}H_2=\overset{sp^2}{C}H-\overset{sp^2}{C}H=\overset{sp^2}{C}H_2$

17. (*a, c, d*): By making two interchanges of atoms or groups of atoms, bring H below the plane of the paper and then find out the sequence of the remaining three atoms or groups in a particular order *i.e.* clockwise or anticlock wise starting from atom with highest atomic number (Br) and moving towards lower atomic numbers (*i.e.* Br ⟶ Cl ⟶ CH_3).



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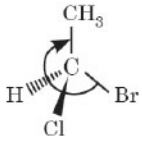
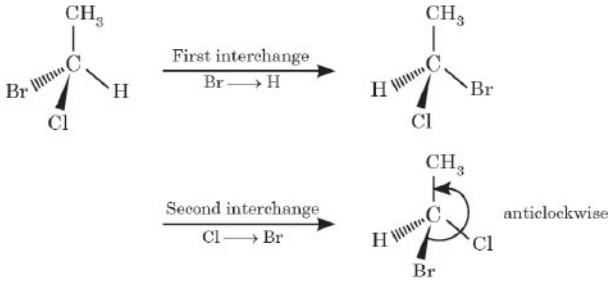
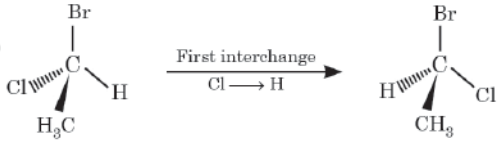
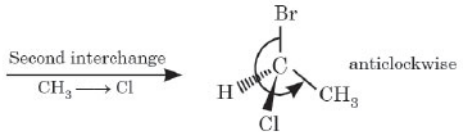
(*b*) 

Clockwise (H is already below the plane of the paper)

(*c*) 

(*d*) 



(*a*), (*c*) and (*d*) have different (anticlockwise) spatial arrangement of atoms or groups of atoms than that given in structure = A (clockwise)

18. (*b*, *c*) : In (*a*) NH_3 and H_2O are nucleophiles but BF_3 is electrophile. In (*d*) $C_2H_5^-$ is nucleophile but $\dot{C}_2H_5$ and $C_2H_5^+$ are electrophiles.

19. (*b*) : II and III are position isomers because they differ in the position of $\rangle C{=}O$ group.

20. (*a*, *c*) : II and III (*i.e.* option *a*) and I and IV (option *c*) are not functional isomers.

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Unit Practice Test

for Board Examination

Time Allowed : 1 Hr. ***Maximum Marks : 25***

1. Write the bond line formula for heptan-4-one. (1)

2. What are the hybridisation states of each carbon in $CH_3—CH=CHCN$? (1)

3. Which of the following is the most stable carbocation ?
$(CH_3)_3CCH^+$, $CH_3C^+HCH(CH_3)_2$, $(CH_3)_3C^+$ (1)

4. In the Lassaigne's test for N in an organic compound, prussian blue colour is formed due to the formation of..... (1)

5. Which of the two : $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why? (1)

6. Draw resonating structures for :
(*i*) C_6H_5OH (*ii*) $C_6H_5NO_2$ (2)

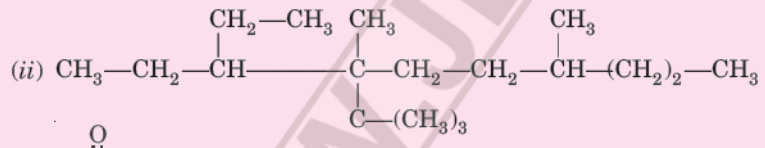
7. 0.32 g of an organochloro compound gave 0.628 g of silver chloride in Carius method of estimation. Calculate the percentage of chlorine present in it. (2)

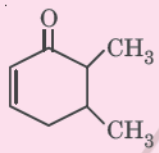
8. Identify the reagents shown underlined in the following equations as nucleophiles or electrophiles:
(*i*) $CH_3COCH_3 + \underline{CN^-} \longrightarrow (CH_3)_2C(OH)CN$
(*ii*) $C_6H_6 + \underline{CH_3CO^+} \longrightarrow C_6H_5COCH_3$
(*iii*) $CH_3COOH + \underline{OH^-} \longrightarrow CH_3COO^- + H_2O$
(*iv*) $CH_3CH_2Br + \underline{SH^-} \longrightarrow CH_3CH_2SH + Br^-$ (2)

9. Discuss the chemistry of Kjeldahl's method for estimation of N in an organic compound. (2)

10. What is the difference between the following terms :
(*i*) distillation
(*ii*) distillation under reduced pressure
(*iii*) steam distillation (3)

11. Give IUPAC names of the following :
(*i*) $HC\equiv C—CH=CH—CH_3$

(*ii*)


(*iii*)


(3)

12. Write the structural formula of the following :
(*i*) Pentanedial
(*ii*) 2-(4-isobutylphenyl) propanoic acid
(*iii*) But-2-en-1-oic acid (3)

13. Explain the following :
(*a*) CCl_4 does not give white precipitate with silver nitrate solution on heating.
(*b*) Nitric acid is added to sodium extract before adding $AgNO_3$ for testing halogens.
(*c*) Alkyl groups act as electron donors when attached to a π-system. (3)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part II of the book.

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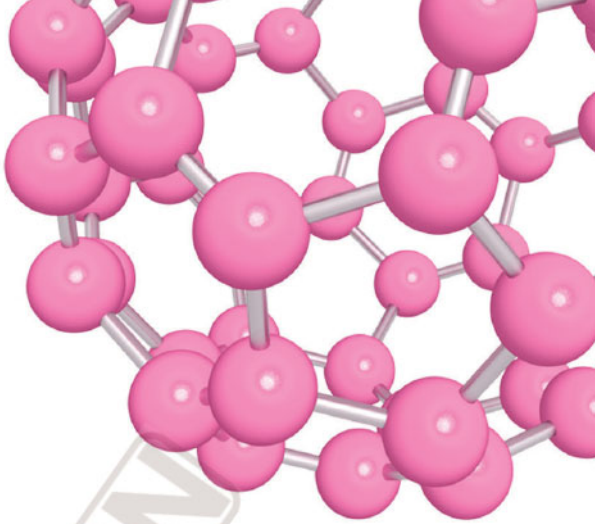
UNIT 13

HYDROCARBONS



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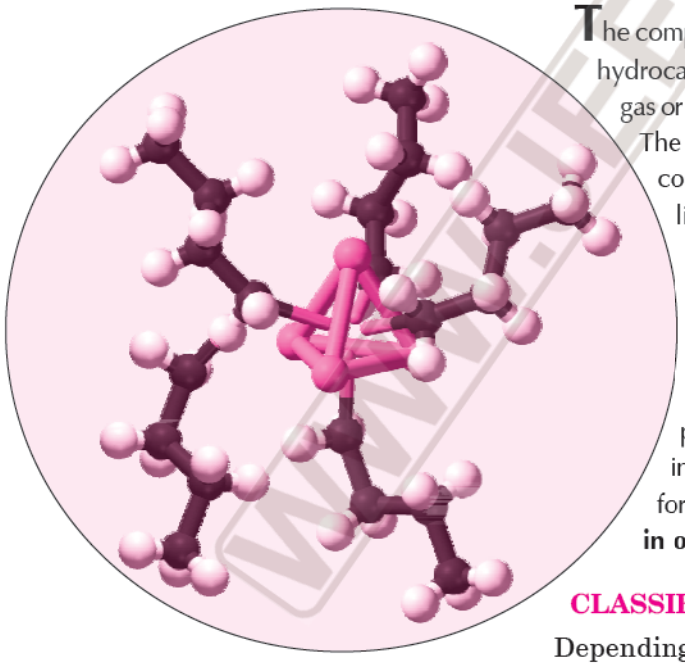

The compounds which contain only carbon and hydrogen are called hydrocarbons. These are obtained mainly from petroleum, natural gas or coal. The hydrocarbons are very important source of energy. The important fuels like petrol, kerosene, coal gas, oil gas, compressed natural gas (CNG), liquefied petroleum gas (LPG), liquefied natural gas (LNG), etc. are all hydrocarbons or their mixtures. Automobiles require fuels like petrol, diesel and CNG. All these fuels contain mixture of hydrocarbons which are sources of energy. The automobiles run by petrol and CNG cause less pollution. Hydrocarbons are also used for the manufacture of polymers such as polythene, polypropene, polystyrene, etc. They are also finding use in manufacture of many dyes and drugs and also as solvents for paints. Thus, **these hydrocarbons play very important role in our daily life.**

CLASSIFICATION OF HYDROCARBONS

Depending upon the types of carbon–carbon bonds present, hydrocarbons can be classified into three main categories :

1. Saturated hydrocarbons
2. Unsaturated hydrocarbons
3. Aromatic hydrocarbons

1. Saturated hydrocarbons

The hydrocarbons which contain only carbon–carbon single bonds **are** called **saturated hydrocarbons**.

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These include open chain hydrocarbons as well as closed chain (cyclic) hydrocarbons.

If different carbon atoms are joined together to form an open chain of carbon atoms with single bonds, they are called **alkanes.**

For example,

$CH_3—CH_3$ Ethane $CH_3—CH_2—CH_3$ Propane $CH_3—CH_2—CH_2—CH_3$ Butane

These compounds are called ***saturated because they have maximum number of bonded hydrogens.***

2. Unsaturated hydrocarbons.

The hydrocarbons which contain carbon–carbon multiple bonds (double bonds or triple bonds or both) are called **unsaturated hydrocarbons.**

Depending upon the multiple bonds (double bond or triple bond) they are further classified as alkenes and alkynes.

Alkenes. *These are hydrocarbons which contain at least one carbon–carbon double bond.* For example,

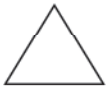
$CH_2 = CH_2$ Ethene $CH_3CH = CHCH_3$ But-2-ene $CH_2 = CH—CH_2—CH_3$ But-1-ene

Alkynes. *These are hydrocarbons which contain at least one carbon-carbon triple bond.* For example,

$HC \equiv CH$ Ethyne $CH_3C \equiv CH$ Propyne $CH_3—C \equiv C—CH_3$ But-2-yne

The saturated and unsaturated hydrocarbons may also contain chains or rings of carbon atoms in their molecules. These are known as **cyclo or cyclic hydrocarbons.**

For example,


Cyclopropane

Cyclobutane

Cyclopentane

Cyclohexane

Cyclopropene

Cyclobutene

Cyclopentene

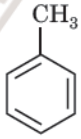
Cyclohexene

3. Aromatic hydrocarbons.

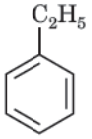
These are hydrocarbons which contain at least one special type of hexagonal ring of six carbon atoms with three double bonds in the alternate positions.

The ring is called **aromatic ring** or **benzene ring.** For example,

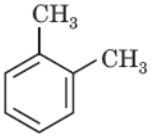
Benzene



Toluene

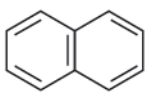


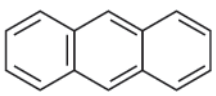
Ethylbenzene



o-Xylene

The aromatic compounds may also contain more than one benzene rings. For example,


Naphthalene


Anthracene

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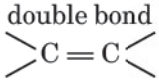
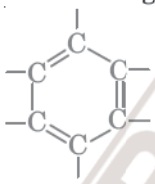
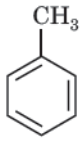
Thus, the types of hydrocarbons may be summarized as :

Hydrocarbon type	Characteristic group	Example
Saturated hydrocarbons :		
Alkanes	Only C—C single bonds	$CH_3CH_2CH_3$ Propane
Cycloalkanes	Only C—C single bonds and a cyclic ring	Cyclopentane
Unsaturated hydrocarbons :		
Alkenes	double bond 	$CH_3—CH=CH_2$ Propene
Cycloalkenes	double bond and a cyclic ring	Cyclohexene
Alkynes	triple bond —C≡C—	$CH_3—C\equiv CH$ Propyne
Aromatic hydrocarbons	benzene ring 	 Methylbenzene

CHEMISTRY OF ALKANES

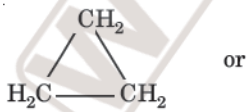
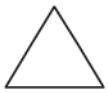
ALKANES

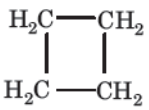
Alkanes are **saturated hydrocarbons containing only carbon-carbon single bonds in their molecules.** They are also called **paraffins** (from Latin words : *parum* meaning little and *affinis* meaning affinity *i.e., little affinity* or *reactivity).* This name is justified because under normal conditions of temperature and pressure, alkanes are inert and do not react with reagents like acids, bases, oxidising agents and reducing agents. However, under drastic conditions *i.e.,* at high temperatures and pressures alkanes do undergo some reactions. The alkanes may be divided as :

1. Open chain or acyclic alkanes. These are simple alkanes without any close chains and have the general formula $\mathbf{C_nH_{2n+2}}$ where n is the number of carbon atoms. For example,

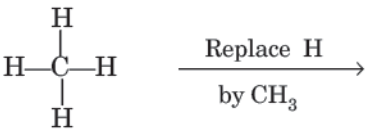
CH_4 Methane $CH_3CH_2CH_3$ Propane $CH_3CH_2CH_2CH_3$ Butane

2. Cycloalkanes or cyclic alkanes. These contain a closed chain or ring in their molecules. They have the general formula $\mathbf{C_nH_{2n}}$. For example,

 or  Cyclopropane

 or Cyclobutane

Methane is the first member of open chain alkanes family. It is a gas found in coal mines and marshy places. The higher member is obtained by replacing one hydrogen atom of methane by carbon and joining the required number of hydrogen atoms to satisfy tetravalence of other carbon atoms. For example, next member obtained is ethane having molecular formula C_2H_6.



or C_2H_6 Ethane

Similarly, higher members are obtained as C_3H_8 (propane), C_4H_{10} (butane), C_5H_{12} (pentane), C_6H_{14} (hexane), etc.

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STRUCTURE OF ALKANES

As already studied, methane, the first member of the family has **tetrahedral** *structure* involving sp^3 hybridisation of carbon.The four sigma bonds are formed by the overlapping of sp^3 hybrid orbital of carbon and 1*s* orbital of hydrogen. In this, carbon atom lies at the centre and the four hydrogen atoms lie at the corners of a regular tetrahedron, making each H—C—H bond angle of 109.5°.

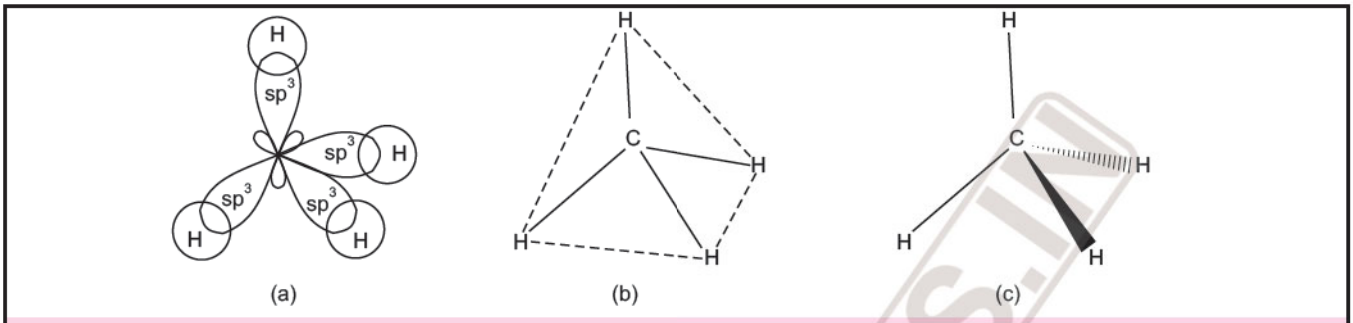
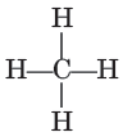


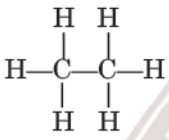
Fig. 1. Spatial arrangement of methane.

The structure of methane molecule is also shown in Fig. 1 (*b*) and Fig. 1 (*c*). In Fig 1 (*c*), the thick or dark lines indicate a C—H bond projecting towards the observer and the dashed line represents a C—H bond away from the observer (behind the plane of the paper) while the two normal lines indicate C—H bonds lying on the plane of the paper. In higher alkanes, the tetrahedra are joined together in which C—C and C—H bond lengths are 154 pm and 112 pm respectively.

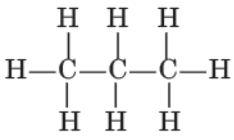
However, for the sake of simplicity, the structures are given in two dimensional or planar representation as shown below . The structures of ethane (C_2H_6) and propane (C_3H_6) are also shown.



Methane



Ethane



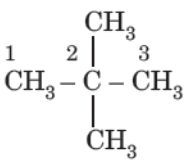
Propane

NOMENCLATURE OF ALKANES

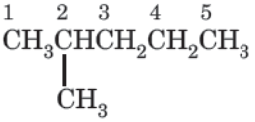
The IUPAC names of some straight chain alkanes are given below:

No. of carbon atoms	Formula	Name
1	CH_4	Methane
2	C_2H_6	Ethane
3	C_3H_8	Propane
4	C_4H_{10}	Butane
5	C_5H_{12}	Pentane
6	C_6H_{14}	Hexane
7	C_7H_{16}	Heptane
8	C_8H_{18}	Octane
9	C_9H_{20}	Nonane
10	$C_{10}H_{22}$	Decane
11	$C_{11}H_{24}$	Undecane
12	$C_{12}H_{26}$	Dodecane
20	$C_{20}H_{42}$	Eicosane
30	$C_{30}H_{62}$	Triacontane

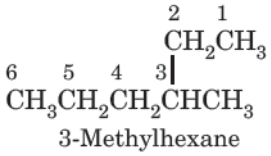
The rules for naming branched chain **alkanes** have been discussed in the previous unit. Some common examples are:



2,2- Dimethylpropane



2-Methylpentane



3-Methylhexane

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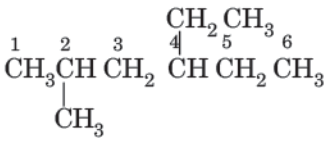
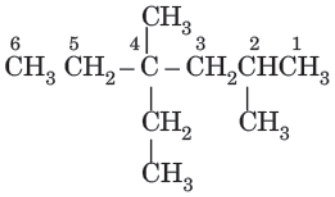
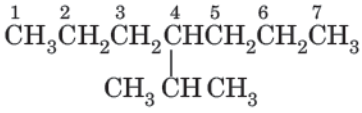


4-Ethyl-2-methylhexane

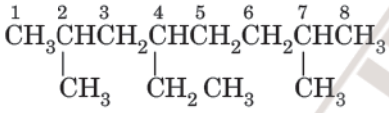
(Lowest set of locants and alphabetical arrangement)



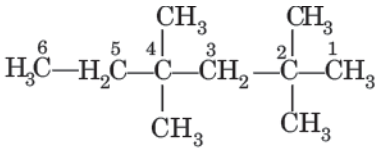
4- Ethyl-2, 4-dimethylhexane



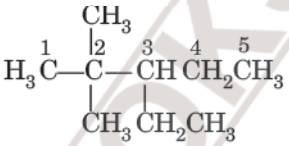
4-(1-methylethyl)heptane
or 4-Isopropylheptane



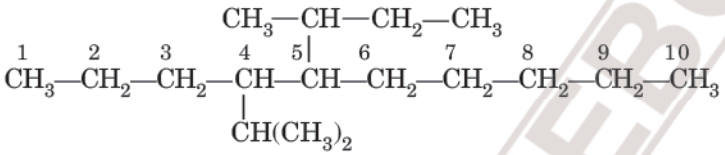
4-Ethyl-2, 7-dimethyloctane



2, 2, 4, 4-Tetramethylhexane

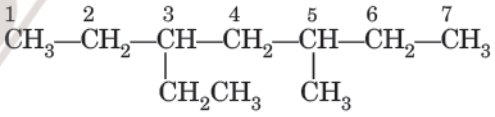


3-Ethyl–2, 2-dimethylpentane

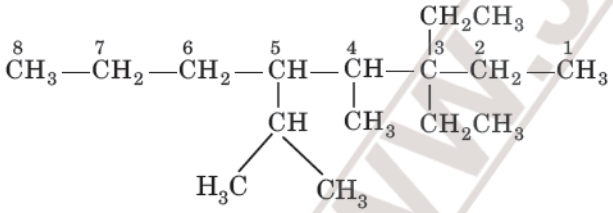


5-*sec*–Butyl-4-isopropyldecane
or 4- (1-methylethyl)-5- (1-methylpropyl)decane

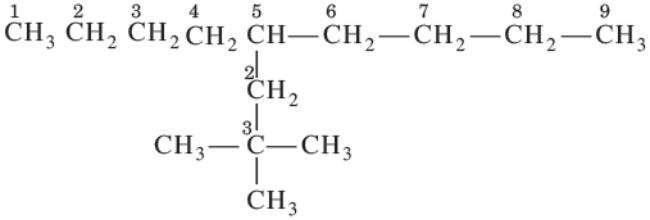
(**Note :** The prefix sec- is ignored while arranging alphabetically, but *iso*propyl is considered as one word).



3-Ethyl-5-methylheptane
(Alphabetical priority order)



3,3-Diethyl-5-isopropyl-4-methyloctane
or 3, 3-Diethyl-4-methyl-5-(1-methylethyl) octane



5-(2,2-Dimethylpropyl)nonane

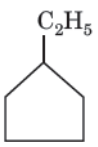
(**Note :** Numbering of the complex substituent begins with the carbon atom attached to the parent chain).

Cycloalkanes are named by using prefix cyclo-to indicate that the compound contains a ring. As already discussed in Unit 12 the common rules for numbering the carbons of ring are as follows :

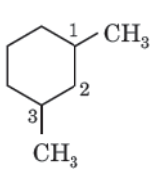
(*i*) *No number is needed if only one group is attached to the ring.*

(*ii*) *For rings with multiple substituents, begin numbering at one substituent and proceed in the direction that gives the lowest numbers to the remaining substituents.*

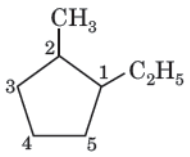
For example,



Ethylcyclopentane



1, 3-Dimethylcyclohexane



1-Ethyl-2-methylcyclopentane

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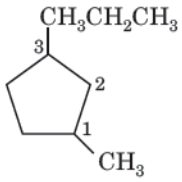
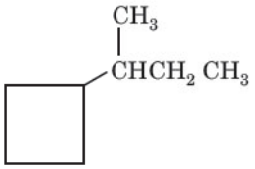
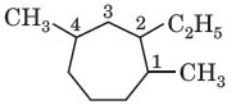


1–Methyl–3–propylcyclopentane

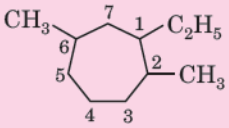


(1–Methylpropyl) cyclobutane

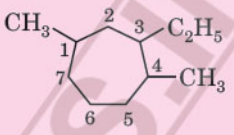


2–Ethyl–1,4–dimethylcycloheptane

Note : The third compound cannot be named as given below because it will give higher number to the substituents.



1-Ethyl-2, 6-dimethyl cycloheptane
↑
Higher



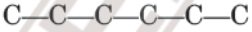
3-Ethyl-1, 4-dimethyl cycloheptane
↑
Higher

Writing structural formula from the name of hydrocarbon

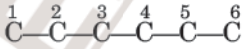
Just as, it is important to write the correct IUPAC name for a given structure, it is also important to write the correct structure from the given name. For this, first of all the longest continuous chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and then finally valence of each carbon atom is satisfied by putting the correct number of hydrogen atoms.

Let us write the structure of **3-ethyl-2,2-dimethylhexane**. This involves the following steps :

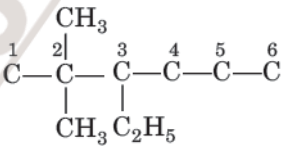
(*i*) Draw the chain of six carbon atoms corresponding to the parent compound hexane.



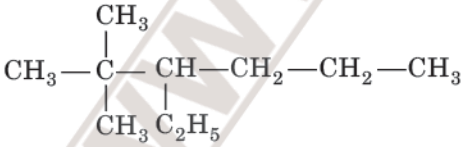
(*ii*) Number the chain of carbon atoms from any end.



(*iii*) Attach ethyl group at carbon 3 and two methyl groups at carbon 2.



(*iv*) Satisfy the valence of each carbon atom (tetravalency) by putting requisite number of hydrogen atoms.



This is the correct structure of 3-ethyl-2,2-dimethylhexane.

SOLVED EXAMPLES

❑ **Example 1.**

Assign IUPAC names of the following compounds :

(*i*) $(H_3C)_4C$

(*ii*) $(H_3C)_2C(C_2H_5)CH_2C(CH_3)_3$

(*iii*) $(CH_3)_3CCH_2C(CH_3)_3$

(*iv*) $CH_3—(CH_2)_4CH(CH_2CH(CH_3)_2)(CH_2)_3CH_3$

(*v*) $(CH_3)_2C(C_2H_5)_2$

(*vi*) tetra-*tert* butylmethane

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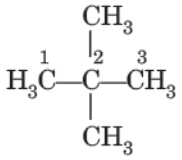
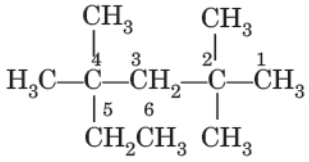
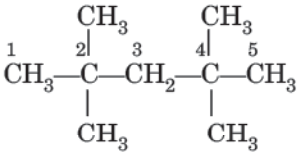
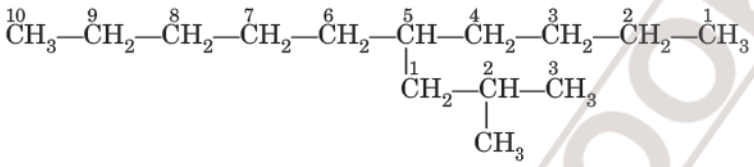
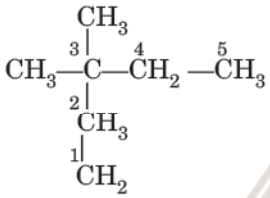
Solution:

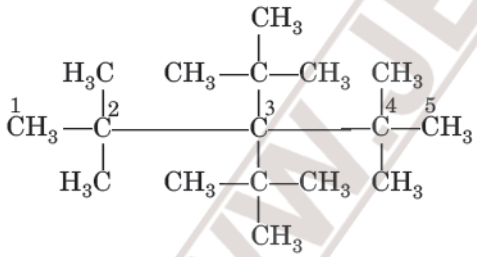
(*i*)  : 2, 2-Dimethylpropane

(*ii*)  : 2, 2, 4, 4–Tetramethylhexane

(*iii*)  : 2, 2, 4, 4 – Tetramethylpentane

(*iv*)  : 5- (2- Methylpropyl)decane

(*v*)  : 3, 3– Dimethylpentane

(*vi*)  : 3,3 -Di-*tert*-butyl-2,2,4,4-tetramethylpentane
or 3,3 -Bis (1, 1-dimethylethyl)2,2,4,4-tetramethylpentane

N.C.E.R.T.

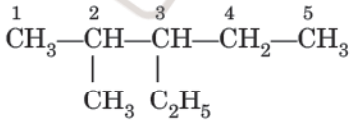
Example 2.

Write the structural formulas for the following compounds whose IUPAC names are given :

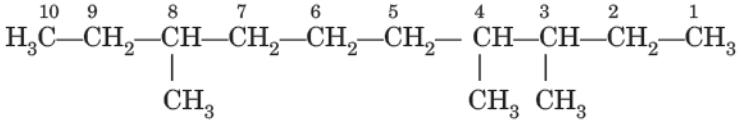
(*i*) 3 - Ethyl-2-methylpentane (*ii*) 3, 4, 8 - Trimethyldecane

(*iii*) 3, 4, 4, 5 - Tetramethylheptane (*iv*) 2, 5- Dimethylhexane

Solution: (*i*) 3 - Ethyl-2-methylpentane



(*ii*) 3, 4, 8-Trimethyldecane



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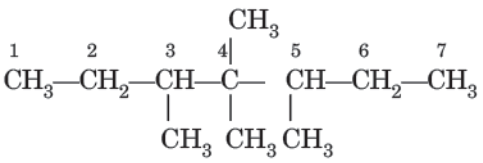
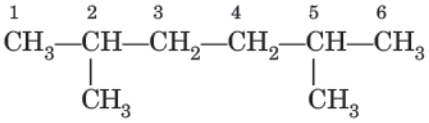
(*iii*) 3, 4, 4, 5-Tetramethylheptane



(*iv*) 2, 5 -Dimethylhexane



❑ Example 3.

The names of some compounds are given below :

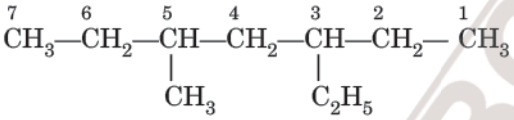
(i) 5-Ethyl-3-methylheptane

(ii) 4-Isopropyl-5-sec-butyldecane

(iii) 2-Ethylpentane

Why are the given names incorrect ?

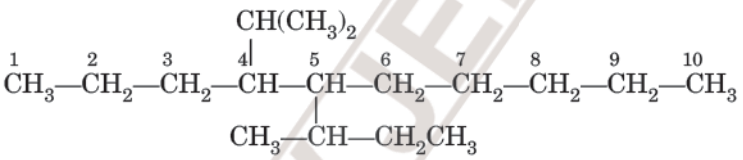
Solution: (*i*)



Ethyl and methyl are at the equivalent positions. The numbering is done from the end which gives lower number to ethyl group (alphabetically). Hence correct name is :

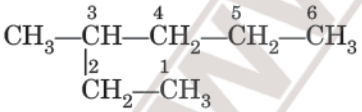
3-Ethyl-5-methylheptane

(*ii*)



Prefix sec is not considered as part of name while iso is considered. Hence correct name is 5-*sec*-Butyl-4-isopropyldecane.

(*iii*)



Longest chain is of 6 carbon atoms and not of five. Hence, the correct name is : 3-Methylhexane.

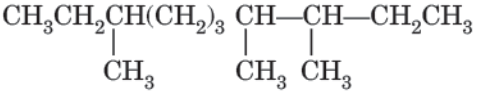
Practice Problems

1. Write the IUPAC names of the following structures :

(*a*) $(C_2H_5)_4C$

(*b*) $(CH_3)_2CH\ CH\ (CH_3)_2$

(*c*)



(*d*) $(CH_3)_3CCH_2C(CH_3)_3$

Ans. (*a*) 3, 3-Diethylpentane

(*b*) 2, 3-Dimethylbutane

(*c*) 3, 4, 8-Trimethyldecane

(*d*) 2, 2, 4, 4-Tetramethylpentane

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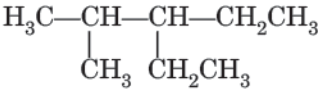
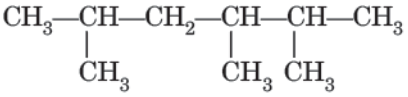
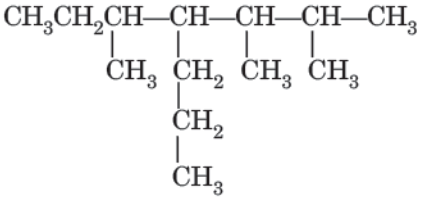
2. Write the structure for the compounds having the IUPAC names :

(*a*) 3-Ethyl-2-methylpentane (*b*) 2, 3, 5-Trimethylhexane

(*c*) 2, 3, 5-Trimethyl-4-propylheptane

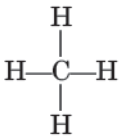
Ans. (*a*) 

(*b*) 

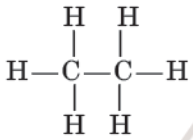
(*c*) 

ISOMERISM IN ALKANES

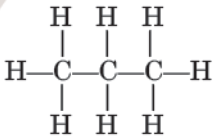
The alkanes show **structural isomerism in which the isomers differ in the skeleton (or chain) of carbon atoms.** For example, the first three members of the family (CH_4, C_2H_6 and C_3H_8) donot exhibit chain isomerism because they have only one structural formula :



Methane (CH_4)

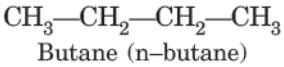


Ethane (C_2H_6)

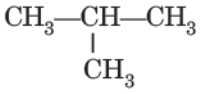


Propane (C_3H_8)

Butane (C_4H_{10}) has **two** structural isomers :

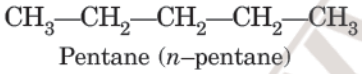


Butane (n–butane)
b.p. 273K

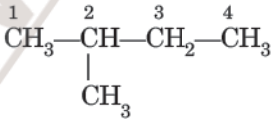


2-Methylpropane (iso–butane)
b.p. 261K

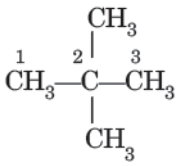
Similarly, **pentane** (C_5H_{12}) has **three isomers**.



Pentane (*n*–pentane)
b.p.309K



2-Methylbutane (isopentane)
b.p. 301K



2,2-Dimethylpropane
(neo–pentane)
b.p. 282.5 K

It is clear that as the number of carbon atoms increases, the number of chain isomers also increases. For example, C_4H_{10} has **two**, C_5H_{12} has **three**, C_6H_{14} has **five**, C_7H_{16} has **nine**, C_8H_{18} has **eighteen** chain isomers. The hydrocarbon $C_{10}H_{22}$ has 75 structural isomers.

Classification of carbon atoms in alkanes.

The carbon atoms in an alkane molecule may be classified into four types as *primary* (1°), *secondary* (2°), *tertiary* (3°) and *quaternary* (4°).

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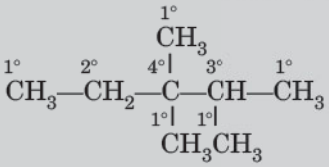
(*i*) A carbon atom attached to one other (or no other) carbon is called **primary carbon** (written as 1° carbon).
(*ii*) A carbon atom attached to two other carbon atoms is called **secondary carbon** (written as 2° carbon).
(*iii*) A carbon atom attached to three other carbon atoms is called **tertiary carbon** (written as 3° carbon)
(*iv*) A carbon atom attached to four other carbon atoms is called **quaternary carbon** (written as 4° carbon).

Hydrogen atoms attached to 1°, 2° and 3° carbon atoms are referred to as primary, secondary and tertiary H atoms respectively. The following example clearly differentiates the various carbon atoms :

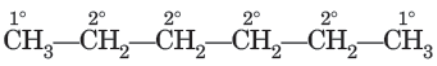


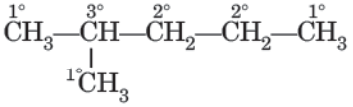
SOLVED EXAMPLES

Example 4.

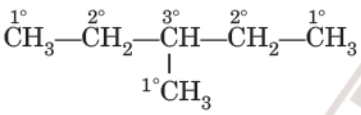
Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Write their IUPAC names and classify each carbon atom as 1°, 2°, 3° or 4°.

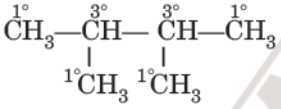
Solution:

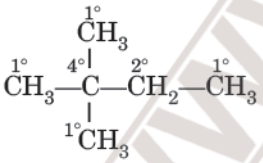
(*i*)  : Hexane

(*ii*)  : 2–Methylpentane

N.C.E.R.T.

(*iii*)  : 3–Methylpentane

(*iv*)  : 2, 3–Dimethylbutane

(*v*)  : 2, 2–Dimethylbutane

Example 5.

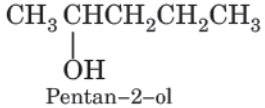
Write the structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11}. Write IUPAC names of alcohols obtained by attachment of —OH groups at different carbons of the chains.

N.C.E.R.T.

Solution:

Structures of C_5H_{11} – group | **Corresponding alcohol**

(*i*) $CH_3CH_2CH_2CH_2CH_2$— | $CH_3CH_2CH_2CH_2CH_2OH$
Pentan-1-ol

(*ii*) | 
Pentan–2–ol

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(*iii*) $CH_3CH_2\underset{|}{C}HCH_2CH_3$

$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_3$

Pentan–3–ol

(*iv*) $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2-$

$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2OH$

3–Methylbutan-1-ol

(*v*) $CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2-$

$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2OH$

2–Methylbutan-1-ol

(*vi*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$

$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$

2-Methylbutan-2-ol

(*vii*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-$

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-OH$

2,2–Dimethylpropan-1-ol

PREPARATION AND PROPERTIES OF ALKANES

Preparation of Alkanes

Alkanes are saturated hydrocarbons with the general formula C_nH_{2n+2}. Alkanes are mostly obtained from petroleum and petroleum by products. Petroleum also called crude oil is pumped from wells. The principal components of crude oil are alkanes. Alkanes are also obtained from natural gas. However, alkanes can also be prepared in the laboratory. Some of the general methods of preparation of alkanes are discussed below :

1. From Unsaturated Hydrocarbons

The unsaturated hydrocarbons (alkenes and alkynes) are converted into alkanes by **catalytic hydrogenation.** In this process dihydrogen gas is passed through alkenes or alkynes in the presence of finely divided catalysts such as Raney nickel (Ni), platinum (Pt) or palladium (Pd). These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen-hydrogen bond.

$$\underset{\text{Alkene}}{\mathbf{RHC=CHR}} + \mathbf{H_2} \xrightarrow[\text{or Raney Ni}]{\text{Pd or Pt}} \underset{\text{Alkane}}{\mathbf{RCH_2CH_2R}}$$

e.g., $\underset{\text{Ethene}}{H_2C=CH_2} + H_2 \xrightarrow[\text{or Raney Ni}]{\text{Pd or Pt}} \underset{\text{Ethane}}{CH_3-CH_3}$

$\underset{\text{Propene}}{CH_3CH=CH_2} + H_2 \xrightarrow[\text{or Raney Ni}]{\text{Pd or Pt}} \underset{\text{Propane}}{CH_3CH_2CH_3}$

$$\underset{\text{Alkyne}}{\mathbf{RC\equiv CR}} + \mathbf{2H_2} \xrightarrow[\text{or Raney Ni}]{\text{Pd or Pt}} \underset{\text{Alkane}}{\mathbf{RCH_2CH_2R}}$$

e.g., $\underset{\text{Ethyne}}{HC\equiv CH} + 2H_2 \xrightarrow[\text{or Raney Ni}]{\text{Pd or Pt}} \underset{\text{Ethane}}{CH_3-CH_3}$

NOTE

Raney nickel is an active form of nickel. It is obtained by alloying 50% Ni and 50% Al (known as Ni-Al alloy). The alloy is heated with aqueous NaOH solution at 50 – 100°C when Al dissolves and Ni is obtained in the form of very fine particles.

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$$\underset{\text{Propyne}}{CH_3–C\equiv CH} + 2H_2 \xrightarrow[\text{or Raney Ni}]{\text{Pd or Pt}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow[523-573\,K]{\text{Ni}} \underset{\text{Ethane}}{CH_3–CH_3}$$

$$\underset{\text{Ethyne}}{CH\equiv CH} + 2H_2 \xrightarrow[523-573\,K]{\text{Ni}} \underset{\text{Ethane}}{CH_3–CH_3}$$

Methane cannot be prepared by this method because starting alkene or alkyne must contain at least two carbon atoms.

It may be noted that platinum, palladium and Raney nickel catalyse the reaction at room temperature. However, higher temperature (523–573 K) and pressure are required with nickel catalysts. ***The hydrogenation reaction of unsaturated hydrocarbons using nickel at a temperature of 523–573K*** is commonly known as **Sabatier and Sendern's reaction or reduction.**

2. From Alkyl halides

Alkyl halides (halogen derivatives of alkanes) can be converted into alkanes by the following methods :

(*a*) Wurtz reaction. When an alkyl halide (usually bromide or iodide) is treated with sodium in dry ether, a symmetrical alkane containing twice the number of carbon atoms of alkyl halide is obtained.

$$\mathbf{R\boxed{X + 2Na + X}R \xrightarrow{\text{Dry ether}} R–R + 2NaX}$$

e.g.,
$$\underset{\text{Ethyl iodide}}{CH_3CH_2\boxed{I + 2Na + I}CH_2CH_3} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 2NaI$$

This method gives alkane with even number of carbon atoms. If two different alkyl halides are taken for preparing an alkane with odd number of carbon atoms, a mixture of products is obtained. For example,

$$RX + 2Na + XR' \xrightarrow[\text{ether}]{\text{Dry}} R–R + R–R' + R'–R'$$

When ethyl bromide and methyl bromide react in the presence of sodium, a mixture of ethane, propane and butane is obtained. *This is because the two alkyl halides not only react with each other but they react amongst themselves also.* For example,

$$\underset{\substack{\text{Methyl}\\\text{bromide}}}{CH_3}\boxed{Br + 2Na + Br}\underset{\text{Ethyl bromide}}{CH_2CH_3} \longrightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} + 2NaBr$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2}\boxed{Br + 2Na + Br}\underset{\text{Ethyl bromide}}{CH_2CH_3} \longrightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 2NaBr$$

$$\underset{\text{Methyl bromide}}{CH_3}\boxed{Br + 2Na + Br}\underset{\text{Methyl bromide}}{CH_3} \longrightarrow \underset{\text{Ethane}}{CH_3CH_3} + 2NaBr$$

Therefore, *Wurtz reaction cannot be used to prepare pure alkanes with odd number of carbon atoms because it is difficult to separate the mixture obtained.*

Two **mechanisms** have been suggested for Wurtz reaction.

(*i*) Through intermediate formation of an organometallic compound :

$$CH_3CH_2Br + 2Na \longrightarrow \underset{\text{Ethyl sodium}}{CH_3CH_2^-Na^+} + NaBr$$

$$CH_3\bar{C}H_2Na^+ + CH_3CH_2Br \longrightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + NaBr$$

(*ii*) Through the formation of intermediate free radicals

$$CH_3CH_2Br + Na \longrightarrow CH_3\dot{C}H_2 + NaBr$$

$$CH_3\dot{C}H_2 + CH_3\dot{C}H_2 \longrightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

(*b*) Corey-House Reaction : Wurtz reaction does not give good yields of unsymmetrical alkanes *i.e.*, containing odd number of carbon atoms. However, both symmetrical and unsymmetrical alkanes can be prepared in good yield by Corey-House reaction. In this reaction, the alkyl halide is first treated with lithium metal in dry ether to form alkyl-lithium which is then allowed to react with cuprous iodide to give lithium dialkyl copper (also called **Gilman reagent**). Lithium dialkyl copper thus obtained is treated with suitable alkyl halide to give desired alkane.

$$\underset{\text{Alkyl halide}}{\mathbf{RX}} + \mathbf{2Li} \xrightarrow{\text{Dry ether}} \underset{\text{Alkyl lithium}}{\mathbf{R—Li}} + \mathbf{LiX}$$

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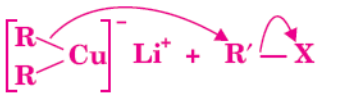
$$\underset{\text{Cuprous iodide}}{2R\text{—}Li + CuI} \longrightarrow \underset{\text{Lithium dialkyl copper}}{R_2CuLi} + LiI$$



$$\longrightarrow \underset{\text{Alkane}}{R\text{—}R'} + \underset{\text{Alkyl copper}}{RCu} + LiX$$

where R and R′ may be same or different alkyl groups. For example,

e.g.,
$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + 2Li \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl lithium}}{CH_3CH_2Li} + LiBr$$

$$2CH_3CH_2Li + CuI \longrightarrow \underset{\text{Lithium diethyl copper}}{[(CH_3CH_2)_2Cu]^-Li^+} + LiI$$

$$[(CH_3CH_2)_2Cu]^-Li^+ + \underset{n\text{-propyl bromide}}{CH_3CH_2CH_2Br} \xrightarrow{\text{Dry ether}} \underset{n\text{-Pentane}}{CH_3CH_2CH_2CH_2CH_3} + \underset{\text{Ethyl copper}}{CH_3CH_2Cu} + LiBr$$

(*c*) Reduction of alkyl halides. Alkyl halides (except fluorides) are reduced to alkanes by suitable reducing agents. For example,

(*i*) *With zinc and HCl*

$$RX + H_2 \xrightarrow{Zn/HCl} RH + HX$$

e.g.,
$$\underset{\text{Chloromethane}}{CH_3Cl} + H_2 \xrightarrow{Zn,\ HCl} \underset{\text{Methane}}{CH_4} + HCl$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + 2H \xrightarrow{Zn/HCl} \underset{\text{Ethane}}{CH_3CH_3} + HBr$$

$$\underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + H_2 \xrightarrow{Zn,\ H^+} \underset{\text{Propane}}{CH_3CH_2CH_3} + HCl$$

(*ii*) *With hydrogen in the presence of platinum or palladium (catalytic hydrogenation)*

$$RX + H_2 \xrightarrow{Pd\ or\ Pt} RH + HX$$

e.g.,
$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + H_2 \xrightarrow{Pd\ or\ Pt} \underset{\text{Ethane}}{CH_3CH_3} + HBr$$

(*iii*) *With hydrogen iodide in the presence of red phosphorus*

$$RBr + 2HI \xrightarrow[423K]{Red\ P} RH + HBr + I_2$$

e.g.,
$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + 2HI \xrightarrow[423\ K]{Red\ P} \underset{\text{Ethane}}{CH_3CH_3} + HBr + I_2$$

The purpose of red phosphorus is to remove iodine. It combines with iodine forming phosphorus triiodide (PI_3). Therefore, it makes the reaction to proceed in the forward direction. If I_2 is not removed, it will convert back alkane into alkyl iodide.

$$2P + I_2 \longrightarrow 2PI_3$$

(*iv*) *By zinc-copper couple and alcohol*

$$2CH_3CH_2OH + \underset{\text{Zn-Cu couple}}{Zn} \xrightarrow{Cu} \underset{\text{Zinc ethoxide}}{(CH_3CH_2O)_2Zn} + 2H$$

$$CH_3CH_2Br + 2H \longrightarrow \underset{\text{Ethane}}{CH_3CH_3} + HBr$$

(*v*) *Alkyl halides are also reduced by chemical reagents such as lithium aluminium hydride ($LiAlH_4$), sodium borohydride ($NaBH_4$), etc.*

$$R\text{—}X \xrightarrow[NaBH_4]{LiAlH_4\ or} \underset{\text{Alkane}}{RH}$$

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It may be noted that in the reduction reaction, nascent hydrogen is no longer considered as the reducing agent. It is believed that there is an electron-transfer from the metal to the substrate followed by the addition of proton from the solvent (ethanol). Therefore, the reduction of alkyl halides with zinc-copper couple may be written as :

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$R{:}\ddot{\underset{\cdot\cdot}{X}}{:} + e^- \longrightarrow R^{\bullet} + :\ddot{\underset{\cdot\cdot}{X}}:^-$$

$$R^{\bullet} \xrightarrow{+e^-} R:^-$$

$$R:^- + C_2H_5OH \longrightarrow R{-}H + {}^-OC_2H_5$$

***(d)* By the use of Grignard reagent.** Alkyl halides react with magnesium metal in diethyl ether to form alkyl magnesium halides. The alkyl magnesium halides are called **Grignard reagents** after the name of their discoverer Victor Grignard, who was awarded Noble Prize in Chemistry in 1912 for the discovery of these versatile reagents. These are highly reactive and can be easily decomposed by water or alcohol to form alkanes. For example,

$$CH_3CH_2Br + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Ethyl magnesium bromide}\\ \text{(Grignard reagent)}}}{CH_3CH_2MgBr}$$

$$CH_3CH_2MgBr + H_2O \longrightarrow \underset{\text{Ethane}}{CH_3CH_3} + \underset{\text{Hydroxy magnesium bromide}}{Mg(OH)Br}$$

In general, the reaction may be represented as :

$$\underset{\substack{\text{Alkyl magnesium}\\ \text{halide}}}{\mathbf{RMgX}} + \underset{\text{Water}}{\mathbf{HOH}} \longrightarrow \underset{\text{Alkane}}{\mathbf{RH}} + \mathbf{Mg(OH)X}$$

3. From Carboxylic acids

Alkanes can be prepared from carboxylic acids by **decarboxylation reaction** and **electrolysis.**

***(i)* Decarboxylation reaction.** When sodium salt of monocarboxylic acid is heated with soda lime (a mixture of NaOH and CaO in the ratio of 3 : 1) at about 630 K, alkane is formed.

$$\underset{\substack{\textbf{Sodium salt}\\ \textbf{of carboxylic acid}}}{\mathbf{R\boxed{COONa + NaO}H}} \xrightarrow[\text{Heat}]{\text{CaO}} \mathbf{RH + Na_2CO_3}$$

In this reaction, *a molecule of CO_2 is removed from carboxylic acid and therefore, the reaction is also called* **decarboxylation.**

The process of removal of a molecule of CO_2 from an organic compound is called **decarboxylation.**

For example,

It may be noted that **the alkanes formed contain one carbon atom less than the carboxylic acid.**

$$\underset{\substack{\text{Sodium}\\ \text{ethanoate}}}{CH_3\boxed{COONa + NaO}H} \xrightarrow[\text{Heat}]{\text{CaO}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

$$\underset{\substack{\text{Sodium}\\ \text{propanoate}}}{CH_3CH_2\boxed{COONa + NaO}H} \xrightarrow[\text{Heat}]{\text{CaO}} \underset{\text{Ethane}}{CH_3CH_3} + Na_2CO_3$$

It may be noted that sodium hydroxide alone could have been used in the above reaction but soda lime is preferred because of the following reasons:

Purpose of CaO in sodalime

(*i*) CaO permits the reaction to be carried out at a relatively higher temperature so that complete decarboxylation is ensured.

(*ii*) Sodium hydroxide is hygroscopic (absorbs moisture from air) in nature but CaO present in soda lime keeps it dry.

For example, methane can be prepared in the laboratory by heating sodium acetate with soda lime (in the ratio of 1 : 4) in a copper tube as shown in Fig. 2. The methane produced is collected over water because it is insoluble in water.

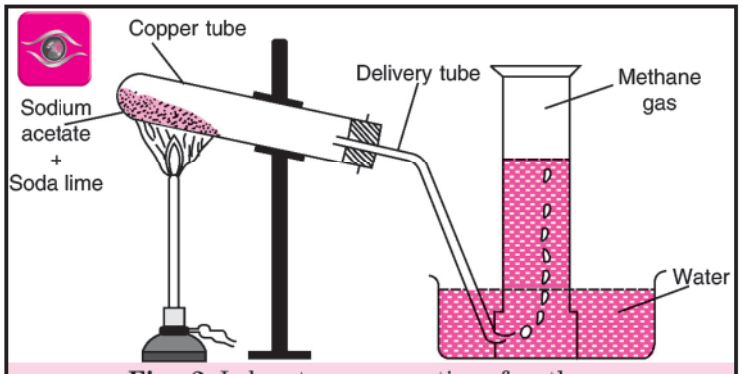

Fig. 2. Laboratory preparation of methane.

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***(ii)* Kolbe's reaction.** When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, alkane is evolved **at the anode.**

$$2CH_3COOK\,(aq) \underset{2e^-}{\overset{\text{Electrolysis}}{\rightleftharpoons}} 2CH_3COO^- + 2K^+$$

At anode :

$$2CH_3COO^- - 2e^- \longrightarrow \underset{\text{(unstable)}}{2CH_3COO}$$

$$2CH_3COO \longrightarrow \underset{\text{Ethane}}{CH_3CH_3} + 2CO_2$$

At cathode : K^+ as well as H^+ ions formed by the electrolysis of water will move towards the cathode. But H^+ ions will be preferentially discharged at the cathode because the discharge potential of H^+ ions is lower than that of K^+ ions. The H^+ ions will be discharged to produce H_2 gas which is liberated at cathode.

$$H^+ + e^- \longrightarrow H$$
$$H + H \longrightarrow H_2$$

The K^+ ions remain in the solution.

Thus, the reaction may be written as :

$$2CH_3COOK + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3CH_3} + 2CO_2 + H_2 + 2KOH$$

In general,

$$\mathbf{2RCOOK + 2H_2O \xrightarrow{Electrolysis} \underset{\text{Alkane}}{R-R} + 2CO_2 + H_2 + 2KOH}$$

Methane cannot be prepared by this method.

Several mechanisms have been proposed for the Kolbe's reaction. The free radical mechanism is the one now favoured as shown below :

$$2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-\overset{\overset{O}{\|}}{C}-O^- + 2Na^+$$

At anode

$$2CH_3-\overset{\overset{O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{\overset{O}{\|}}{C}-\dot{O}:$$

Acetate ion → Acetate free radical

$$2CH_3\cdot : \overset{\overset{O}{\|}}{C} - \dot{O}: \longrightarrow \underset{\text{Methyl free radical}}{2\dot{C}H_3} + 2\overset{\overset{O}{\|}}{C}=O\ (2CO_2)$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow \underset{\text{Ethane}}{CH_3CH_3}$$

At cathode

$$H_2O + e^- \longrightarrow {}^-OH + \underset{\text{Free radical}}{\dot{H}}$$

$$\dot{H} + \dot{H} \longrightarrow H_2\uparrow$$

Limitation. Like Wurtz reaction, Kolbe's electrolysis method can be used to prepare only alkanes with even number of carbon atoms and not alkanes with odd number of carbon atoms.

***(iii)* Reduction of carboxylic acids.** The carboxylic acids are reduced to alkanes by hydroiodic acid. In this reaction, the –COOH group is reduced to $-CH_3$ group. For example,

$$\mathbf{RCOOH + 6HI \xrightarrow{Reduction} \underset{\text{Alkane}}{RCH_3} + 2H_2O + 3I_2}$$

e.g.,
$$\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \xrightarrow{\text{Reduction}} \underset{\text{Ethane}}{CH_3CH_3} + 2H_2O + 3I_2$$

e.g.,
$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} + 6HI \xrightarrow{\text{Reduction}} \underset{\text{Propane}}{CH_3CH_2CH_3} + 2H_2O + 3I_2$$

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Thus, to **sum up,** carboxylic acids are converted to alkanes as :

$$R—COONa \xrightarrow[CaO]{NaOH} RH$$

$$R—COOK \xrightarrow{Electrolysis} R—R$$

$$R—COOH \xrightarrow[HI]{Reduction} R—CH_3$$

Physical Properties of Alkanes

The important physical properties of alkanes are discussed below :

1. Nature. Alkanes are almost non-polar molecules because of the covalent nature of C—C and C—H bonds and due to very little difference of electronegativity between carbon and hydrogen atoms. Therefore, the molecules are held only by weak van der Waals forces (also called London dispersion interactions). The weak intermolecular forces depend only upon the size (surface area) and the structure of molecules. Due to the weak forces, the C_1 to C_4 alkanes are gases, the next thirteen alkanes from C_5 to C_{17} are liquids and the higher members with more than 18 carbon atoms are solids at 298 K.

2. Boiling point. Alkanes have generally low boiling points because these are non-polar and the molecules are held together only by weak van der Waals forces. With the increase in the number of carbon atoms, the molecular size increases and therefore, the magnitude of van der Waals forces also increases. Consequently, the boiling points increase with increase in number of carbon atoms.

It has been observed that each carbon added to the chain increases the boiling point by 20-30 K. The boiling points of *n*-alkanes with increase in number of carbon atoms per molecule of the homologous series are shown in Fig. 3. The difference between two lower homologous is larger than that for the higher ones.

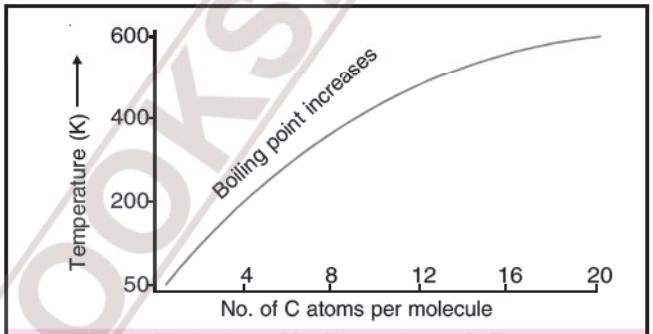
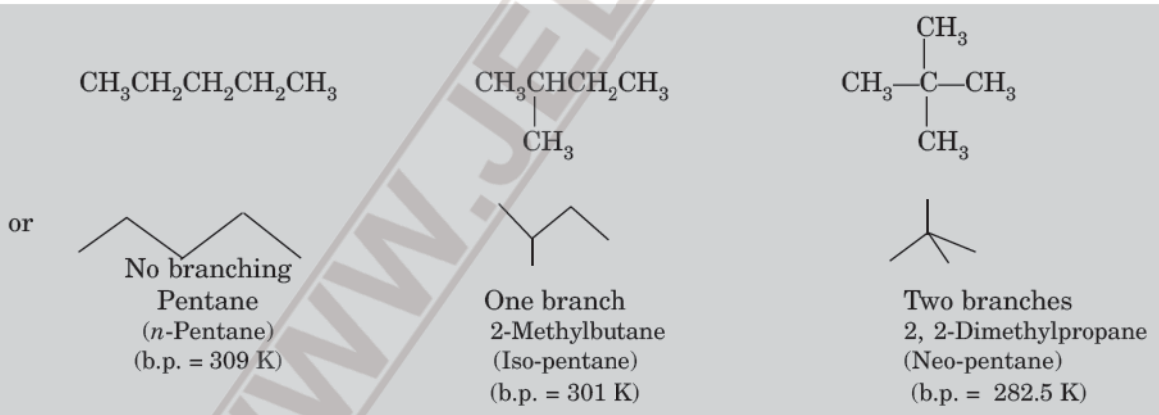


Fig. 3. Variation of boiling points of alkane with increase in number of C atoms.

The branched chain compounds have lower boiling points than the corresponding straight chain isomers. For example, the boiling points of isomeric pentanes are :



This is due to the fact that branching of the chain makes the molecule more compact and thereby decreases the surface area. Therefore, the intermolecular attractive forces which depend upon the surface area, also become small in magnitude on account of branching. Consequently, *the boiling points of the branched chain alkanes are less than the straight chain isomers.*

3. Melting point. The melting points of alkanes do not show regular variation with increase in molecular size. It has been observed that, in general, *the alkanes with even number of carbon atoms have higher melting points as compared to the immediately next lower alkanes with odd number of carbon atoms.* For example,

Alkane	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$
m.p. (K)	85.3	134.6	143.3	178.5	182.4	216.2	222.0	243.3

The melting point of a substance depends not only upon the size and shape of the molecules but also upon the packing of its molecules in the crystal lattice. In n-alkanes, the carbon atoms are arranged in a zig zag chain. Therefore, in n-alkanes containing an odd number of carbon atoms, the two terminal methyl groups lie

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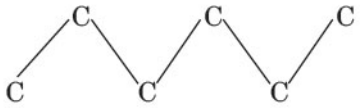
on the same side of zig zag chain. On the other hand, in case of *n*-alkanes containing an even number of carbon atoms, the two terminal methyl groups lie on the opposite side of the zig zag chain as shown below:

Odd numbered carbon atoms



Even numbered carbon atoms

It is clear that the alkanes with even number of carbon atoms have more *symmetrical structures* and result in closer packing in the crystal structure as compared to alkanes with odd number of carbon atoms. Therefore, the van der Waals forces of attraction in the former are more and the melting points are higher as compared to the alkanes with odd number of carbon atoms.

4. Solubility. The solubility of a compound is governed by the principle that *like dissolves like.* Therefore, alkanes being non-polar in nature, are expected to be insoluble in water (polar solvent). They dissolve in non-polar solvents such as ether, benzene, carbon tetrachloride etc. The solubility generally decreases with increase in molecular mass. As we know, petrol is a mixture of hydrocarbons and is used as a fuel for automobiles. Petrol and lower fractions of petroleum are also used for dry cleaning of clothes to remove grease stains. Grease is non-polar and hence dissolves in non-polar petrol and other lower fractions of petroleum. Hence, grease is hydrophobic in nature.

5. Density. Alkanes are lighter than water. The density increases with the increase in the number of the carbon atoms.

The melting points and boiling points of some alkanes are given in Table 1.

Table 1. Melting and boiling points of alkanes

Molecular formula	Name	Molecular mass (u)	Boiling point (K)	Melting point (K)
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.8	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_5H_{12}	2, 2-Dimethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5
C_7H_{16}	Heptane	100	371.4	182.4
C_8H_{18}	Octane	114	398.8	216.2
C_9H_{20}	Nonane	128	423.8	222.0
$C_{10}H_{22}$	Decane	142	447.2	243.3
$C_{20}H_{42}$	Icosane	282	615.0	236.2

Chemical Properties of Alkanes

Alkanes are saturated compounds and the C—C and C—H bonds are non-polar. Therefore, they are **very less reactive** and behave as inert towards acids, bases, oxidising and reducing agents. However, they undergo some replacement or substitution reactions in which the hydrogen atom of alkanes is substituted by other atoms or group of atoms.

Some important chemical reactions of alkanes are discussed below :

1. Substitution Reactions of Alkanes

The **substitution reactions** *are those* ***in which an atom or group of atoms in a molecule is replaced by some other atom or group of atoms.*** Alkanes undergo substitution reactions in which one or more hydrogen atoms are replaced or substituted by different atoms or groups such as halogen atom (Cl, Br or I), nitro group (—NO_2) or sulphonic acid (—SO_3H) group. Some of these are discussed below :

(*a*) **Halogenation.** This involves the replacement of one or more atoms of alkanes by the corresponding number of halogen atoms. For example,

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Chlorination of alkanes is carried out by treating alkane with chlorine in the presence of diffused sunlight or ultraviolet light or by heating it to a temperature between 523-773 K.

$$CH_4 + Cl_2 \xrightarrow[\text{Heat}]{\text{Light or}} \underset{\text{Chloromethane (Methyl chloride)}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Dichloromethane (Methylene dichloride)}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Trichloromethane (Chloroform)}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Tetrachloromethane (Carbon tetrachloride)}}{CCl_4} + HCl$$

During the reaction, a mixture of different halogenated products is formed and the various halogen derivatives have to be separated from the mixture.

Bromination occurs similarly but less *rapidly.*

Iodination is carried out by heating alkane with iodine in the presence of some oxidising agent like iodic acid (HIO_3) or nitric acid (HNO_3) or mercuric oxide (HgO) which oxidises HI formed during the reaction. If HI is not oxidised, being a strong reducing agent, it will make the reaction reversible in nature.

$$\underset{\text{Methane}}{CH_4} + I_2 \overset{\text{Heat}}{\rightleftharpoons} \underset{\text{Iodomethane (Methyl iodide)}}{CH_3I} + HI$$

$$5HI + HIO_3 \xrightarrow{\text{Heat}} 3H_2O + 3I_2$$

or

$$2HI + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + I_2$$

Fluorination of alkanes takes place explosively resulting even in the rupture of C—C and C—H bonds forming a mixture of products. Therefore, fluorination of alkanes can be carried out in controlled conditions. It is carried out by diluting fluorine with an inert gas such as nitrogen or argon. Without special precautions, the mixtures of fluorine and alkane explode.

Alternatively, alkyl halides are more conveniently prepared by heating suitable chloroalkanes with AsF_3, SbF_3, Hg_2F_2, etc. For example,

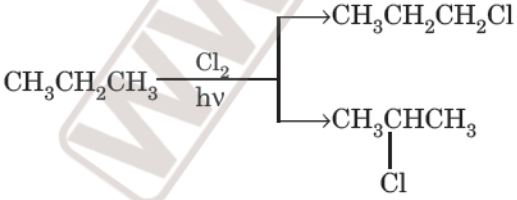
$$2CH_3CH_2Cl + \underset{\text{Mercurous fluoride}}{Hg_2F_2} \longrightarrow \underset{\text{Fluoroethane}}{2CH_3CH_2F} + Hg_2Cl_2$$

This reaction is called Swarts **reaction**.

The reactivity of halogenation is, therefore,

fluorine > chlorine > bromine > iodine

Higher alkanes, on halogenation give different isomers of halogen derivatives. For example, chlorination of propane gives a mixture of 1-chloropropane and 2-chloropropane as :



1-Chloropropane (45%)
(*n*-Propyl chloride)

2-Chloropropane (55%)
(Isopropyl chloride)

The rate of replacement of hydrogens of alkanes is :
3° > 2° > 1°

Mechanism :

Halogenation of alkanes proceed through the formation of free radicals. Therefore, it is also called **free radical substitution reaction**. The reaction proceeds in the following steps :

1. Chain initiation step. The first step involves the homolytic dissociation of chlorine molecule into two chlorine atoms or free radicals. The chlorine molecule absorbs light or heat energy, which breaks the bonds between the atoms. This *step initiates the reaction* and is called **chain initiation step**.

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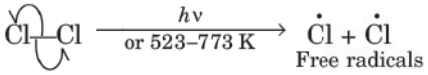
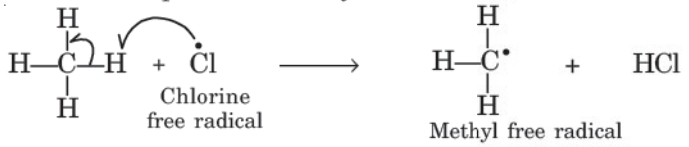


Initiation step

2. Chain propagating steps. The chlorine free radical produced in step (*i*) attacks methane molecule and forms HCl molecule and produces methyl free radical.

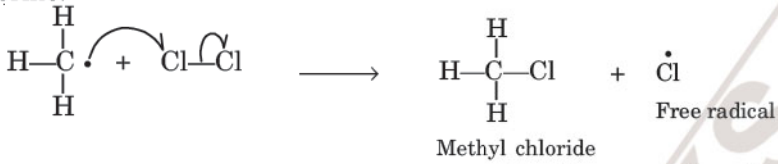
(*i*)



Propagation step

The methyl free radical further reacts with Cl_2 molecule to form methyl chloride (product) and produces free radical chlorine.

(*ii*)



Propagation step

It is clear that steps (*i*) and (*ii*) consume one free radical and generate the other free radical and therefore, they propagate the reaction. These steps are called **chain propagating steps.** These are repeated again and again till whole of CH_4 and Cl_2 have reacted to form methyl chloride. Such a sequence of reactions is **chain reaction.**

3. Chain terminating steps. In addition to above reactions, there are some reactions which remove the reactive species (free radicals) needed for the propagation of the reaction. These are called **chain terminating reactions.** Some of these chain terminating steps are :

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$$

$$\dot{CH}_3 + \dot{CH}_3 \longrightarrow CH_3CH_3$$

$$\dot{CH}_3 + \dot{Cl} \longrightarrow CH_3Cl$$

Thus , these different steps lead to the formation of methyl chloride. As the reaction progresses, more and more methyl chloride is formed.

The chlorine free radical can also abstract a hydrogen atom from methyl chloride forming a substituted methyl free radical. This will react with Cl_2 molecule to form methylene chloride.

$$CH_3Cl + \dot{Cl} \longrightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl_2 \longrightarrow \underset{\text{Methylene chloride}}{CH_2Cl_2} + \dot{Cl}$$

Similarly, trichloromethane and tetrachloromethane may be formed as represented below :

$$CH_2Cl_2 + \dot{Cl} \longrightarrow \dot{C}HCl_2 + HCl$$

$$\dot{C}HCl_2 + Cl_2 \longrightarrow \underset{\text{Trichloromethane}}{CHCl_3} + \dot{Cl}$$

$$CHCl_3 + \dot{Cl} \longrightarrow \dot{C}Cl_3 + HCl$$

$$\dot{C}Cl_3 + Cl_2 \longrightarrow \underset{\text{Tetrachloromethane}}{CCl_4} + \dot{Cl}$$

(*b*) **Nitration.** This involves **the replacement of a hydrogen atom of alkane with —NO_2 group.** At room temperature, alkanes do not react with nitric acid. However, nitration of higher alkanes (hexane or higher) is carried out by boiling alkane with nitric acid.

$$\underset{\text{Hexane}}{C_6H_{14}} + HNO_3 \longrightarrow \underset{\text{Nitrohexane}}{C_6H_{13}NO_2} + H_2O$$

The nitration of lower alkanes can be carried out in **vapour phase** by heating to very high temperature (723-773 K).

$$\underset{\text{Methane}}{CH_4} + HNO_3 \xrightarrow{723\text{-}773\ K} \underset{\text{Nitromethane}}{CH_3NO_2} + H_2O$$

$$\underset{\text{Ethane}}{CH_3CH_3} + HNO_3 \xrightarrow{723\text{-}773\ K} \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + H_2O$$

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However in the vapour phase nitration, the C—C bonds of alkanes may break because of higher temperature giving a mixture of nitrated products. For example, vapour phase nitration of ethane gives a mixture of nitromethane and nitroethane.

$$\underset{\text{Ethane}}{CH_3-CH_3} + HNO_3 \xrightarrow[723\text{-}773\ K]{\text{Vapour phase}} \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2} + H_2O$$

Higher alkanes give even more complicated mixtures. For example, propane gives the following products:

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[673K]{\text{Fuming } HNO_3} \underset{\substack{\text{1-Nitropropane}\\(25\%)}}{CH_3CH_2CH_2NO_2} + \underset{\substack{\text{2–Nitropropane}\\(40\%)}}{CH_3-\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH_3} + \underset{\text{Nitroethane (10\%)}}{CH_3CH_2NO_2}$$

$$+ \underset{\text{Nitromethane (25\%)}}{CH_3NO_2} + \text{other oxidation products } (CO_2,\ NO_2,\ H_2O, \text{etc.})$$

The order of reactivity of different hydrogens in this reaction is :

$$3^\circ > 2^\circ > 1^\circ$$

The reaction is believed to occur as :

$$HONO_2 \xrightarrow[\text{Homolytic fission}]{673\ K} H\dot{O} + N\dot{O}_2$$

$$R-H + \dot{O}H \longrightarrow \dot{R} + H_2O$$

$$\dot{R} + \dot{N}O_2 \longrightarrow RNO_2$$

(*c*) **Sulphonation.** ***This involves the replacement of a hydrogen atom of alkane by —SO_3H group.*** The alkanes undergo sulphonation with fuming sulphuric acid at high temperatures (675-725K). The higher alkanes (containing six or more carbon atoms) undergo sulphonation to give alkane sulphonic acids. The ease of substitution is $3^\circ > 2^\circ > 1^\circ$.

$$C_6H_{14} + H_2SO_4 \xrightarrow[675\ K]{SO_3} \underset{\text{Hexane sulphonic acid}}{C_6H_{13}SO_3H} + H_2O$$

$$\underset{\text{2–Methylpropane}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-H} + H_2SO_4 \xrightarrow[675K]{SO_3} \underset{\text{2–Methylpropane-2-sulphonic acid}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-SO_3H} + H_2O$$

The reaction is believed to occur as :

$$HO-SO_3H \xrightarrow{675\ K} H\dot{O} + \dot{S}O_3H$$

$$R-H + H\dot{O} \longrightarrow \dot{R} + H_2O$$

$$\dot{R} + \dot{S}O_3H \longrightarrow \underset{\text{Alkane sulphonic acid}}{R-SO_3H}$$

Lower alkanes particularly methane, ethane, etc. do not give this reaction.

2. Oxidation

The alkanes undergo oxidation reactions under special conditions to form a variety of products :

(*a*) **Complete oxidation or combustion.** Alkanes on heating in the presence of air or dioxygen are completely oxidised to carbon dioxide and water with the evolution of large amount of heat. This process is called **combustion**.

They burn in air or oxygen giving carbon dioxide, water and liberate large quantities of heat.

$$\underset{\text{Methane}}{CH_4\,(g)} + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l) \quad ; \quad \Delta H^\circ = -890.4\ kJ\ mol^{-1}$$

$$\underset{\text{Ethane}}{2C_2H_6\,(g)} + 7O_2(g) \longrightarrow 4CO_2\,(g) + 6H_2O\,(l) \quad ; \quad \Delta H^\circ = -1580.0\ kJ\ mol^{-1}$$

$$\underset{\text{Butane}}{C_4H_{10}\,(g)} + \frac{13}{2}O_2(g) \longrightarrow 4CO_2\,(g) + 5H_2O\,(l) \quad ; \quad \Delta H^\circ = -2875.84\ kJ\ mol^{-1}$$

The general combustion reaction for any alkane may be written as :

$$\underset{\text{Alkane}}{\mathbf{C_nH_{2n+2}}} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow n\mathbf{CO_2} + (n+1)\,\mathbf{H_2O}$$

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During the combustion, a large amount of heat is evolved and therefore, the hydrocarbons are used as fuels. The cooking gas, which is often called L.P.G. (liquefied petroleum gas) is a mixture of propane and butane.

(*b*) **Incomplete combustion.** When the combustion is carried out in insufficient supply of oxygen, they form carbon monoxide and carbon (carbon black or soot). For example,

$$2CH_4(g) + 3O_2(g) \xrightarrow{\text{Burn}} 2CO(g) + 4H_2O(l)$$

$$CH_4(g) + \underset{\text{limited}}{O_2(g)} \longrightarrow \underset{\text{Carbon black}}{C(s)} + 2H_2O(l)$$

The carbon black is used in the manufacture of black ink, black pigments, paints, polishes, etc.

(*c*) **Controlled oxidation or catalytic oxidation.** The controlled oxidation of alkanes in the presence of **suitable catalysts** gives different products :

(*i*) When a mixture of methane and oxygen in the molar ratio of 9 : 1 is compressed to about 100 atmospheres and passed through copper tubes at 523 K, methane is oxidised to methanol.

$$2CH_4 + O_2 \xrightarrow[100\text{ atm}]{\text{Cu, 523 K}} \underset{\substack{\text{Methanol}\\\text{(Methyl alcohol)}}}{2CH_3OH}$$

(*ii*) When methane is mixed with oxygen and passed through heated molybdenum oxide (Mo_2O_3), under pressure it is oxidised to **methanal.**

$$CH_4 + O_2 \xrightarrow[\text{Heat}]{Mo_2O_3} \underset{\substack{\text{Methanal}\\\text{(Formaldehyde)}}}{HCHO} + H_2O$$

(*iii*) Alkanes are oxidised to carboxylic acids by silver oxide (Ag_2O).

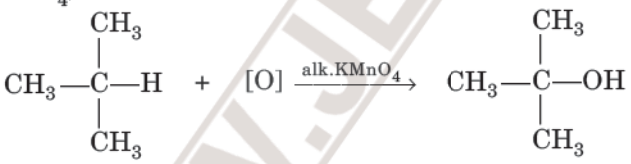
$$\underset{\text{Alkane}}{2R—CH_3} + 3O_2 \xrightarrow{Ag_2O} \underset{\text{Carboxylic acid}}{2RCOOH} + 2H_2O$$

e.g., $$2CH_3CH_3 + 3O_2 \longrightarrow \underset{\text{Acetic acid}}{2CH_3COOH} + 2H_2O$$

Oxidation of alkanes with manganese acetate also gives carboxylic acids :

$$\underset{\text{Ethane}}{2CH_3CH_3} + 3O_2 \xrightarrow[\text{Heat}]{(CH_3COO)_2Mn} \underset{\text{Ethanoic acid}}{2CH_3COOH} + 2H_2O$$

(*iv*) Alkanes having tertiary hydrogen atom can be oxidised to alcohols in the presence of potassium permanganate ($KMnO_4$).



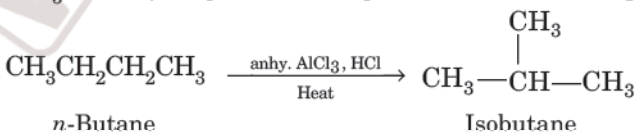
2-Methylpropane (Isobutane) — 2-Methylpropan-2-ol (*tert*-Butyl alcohol)

3. Action of steam. On passing a mixture of steam and methane over heated nickel (supported over alumina, Al_2O_3) catalyst at 1273 K, methane is oxidised to carbon monoxide and hydrogen is evolved.

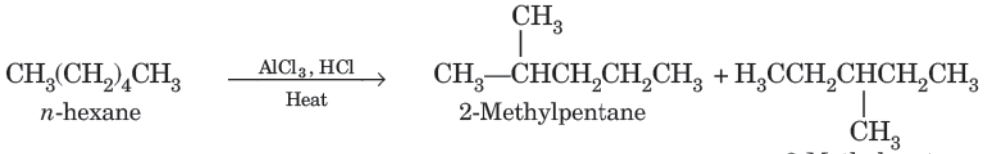
$$CH_4 + \underset{\text{Steam}}{H_2O} \longrightarrow CO + 3H_2$$

This reaction is used for the industrial preparation of hydrogen from natural gas.

4. Isomerisation. Alkanes isomerise to branched chain alkanes when heated with anhydrous aluminium chloride ($AlCl_3$) and hydrogen chloride gas at 573 K under a pressure of about 30–35 atmosphere.



n-Butane — Isobutane



n-hexane — 2-Methylpentane — 3-Methylpentane

The process of isomerisation has been of immense use in petroleum industry for raising the octane number of a petroleum fraction.

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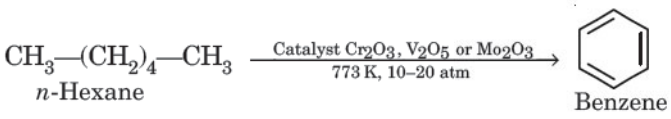
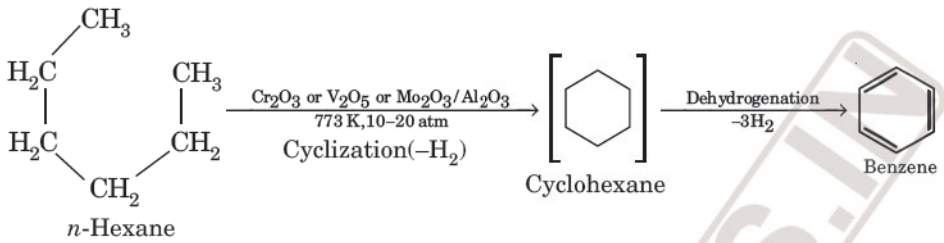
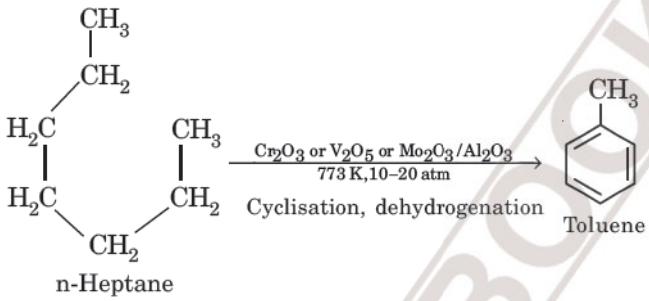
5. Aromatization. The alkanes containing six or more carbon atoms when heated at about 773 K under high pressure of 10–20 atm in the presence of catalysts like oxides of chromium, molybdenum or vanadium supported on alumina get converted to aromatic compounds. This process is called **aromatization** or **reforming** and is discussed later.



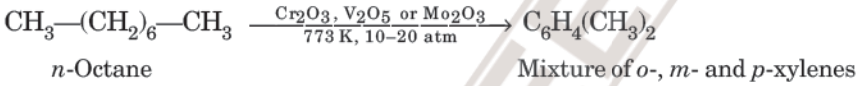
or



Similarly, heptane gives toluene (methyl benzene),



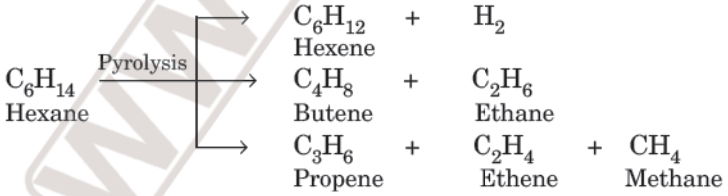
Under similar conditions *n*-octane gives a mixture of *o*-, *m*- and *p*-xylenes.



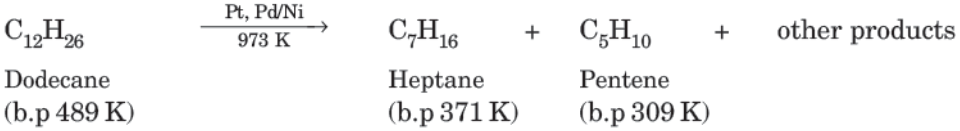
6. Thermal decomposition or pyrolysis. When higher alkanes are heated to high temperatures (about 700–800 K) in the presence of alumina or silica catalysts, the alkanes break down to lower alkanes and alkenes. For example,

The reaction is called **fragmentation** or **cracking** or **pyrolysis.**

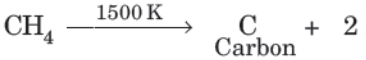
Pyrolysis of hexane gives following products :



Pyrolysis of alkanes is believed to be a free radical reaction. Catalytic cracking of petrol or kerosene oil is employed for the production of oil gas or petrol gas. For example, dodecane a constituent of kerosene oil, on heating to 973 K in the presence of platinum, palladium or nickel gives a mixture of heptane, pentene and other products:



When methane is heated to a high temperature of the order of 1500 K, it breaks down to its elements.



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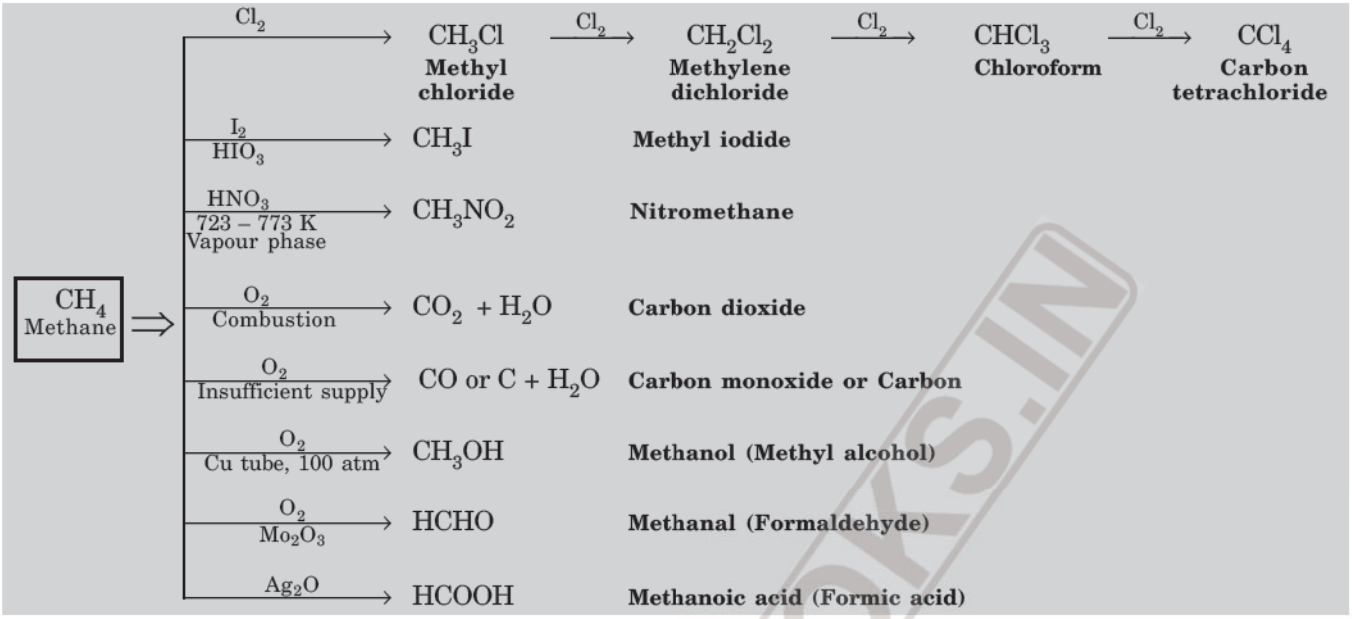
The important chemical reactions of **methane** are summarized below :



CONFORMATIONS OF HYDROCARBONS

The carbon–carbon single bond in alkanes is formed when a sp^3 hybrid orbital of one carbon atom overlaps with a sp^3 hybrid orbital of another carbon atom. It is a sigma bond and has cylindrical symmetry. As a result, atoms involved in single bonds can rotate about the axis of the bond without affecting the overlap of the orbitals that forms the bond. In other words, *rotation about carbon-carbon bond is quite free.*

C — C σ bond

Free rotation around C — C σ bond

Therefore, a large number of different spatial arrangements of the atoms or groups of atoms attached to the carbon atoms are possible. These different spatial arrangements are called **conformational isomers *(conformers)*** or **rotational isomers *(rotamers).*** Thus,

the different arrangements of atoms in space which can be obtained due to rotation about carbon–carbon single bond *are called* ***conformations.***

It may be noted that rotation around a C—C sigma bond is not completely free. It is in fact hindered by an energy barrier of 1 to 20 kJ mol^{-1} in different bonds. There is a possibility of weak repulsive interactions between the bonds or electron pairs of the bonds on adjacent carbon atoms. Such type of repulsive interaction is known as **torsional strain.**

Conformations of Ethane

In ethane molecule (CH_3—CH_3), the two carbon atoms are bonded by a single covalent bond. If one of the carbon atoms (methyl group) is kept fixed and the other is rotated about the C—C bond, an infinite number of arrangements of the hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms of the second carbon atom are possible. These infinite number of different arrangements are called conformations.

To represent these conformations, we can draw three dimensional pictures. However, chemists represent conformations in two simple ways as shown in Figs. 4 and 5 . These are :

(a) Sawhorse representation (b) Newman projection

***(a)* Sawhorse representation.** In this projection, the molecule is viewed along the axis of the model from an oblique angle . The central carbon–carbon bond (C–C) is drawn as a straight line slightly tilted to right for the sake

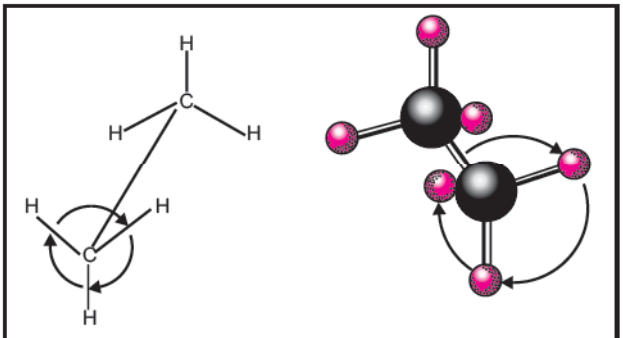


Fig. 4. Rotation around C–C single bond in ethane.

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of clarity. The front carbon is shown as the lower left hand carbon and the rear carbon is shown as the upper right hand carbon. The three bonds around each carbon atom (C–H in ethane or C–C in higher alkanes) are shown by three lines (Fig. 4).

***(b)* Newman projection.** This is a simple method to represent the conformations. In this method, the molecule is viewed from the front along the carbon-carbon bond axis. The two carbon atoms forming the σ-bond are represented by two circles; one behind the other so that only the front carbon is seen. The front carbon atom is shown by a point whereas the carbon further from the eye is represented by the circle. Therefore, the C—H bonds of the front carbon are depicted from the centre of the circle while C—H bonds of the back carbon are drawn from the circumference of the circle at an angle of 120° to each other (Fig. 5).

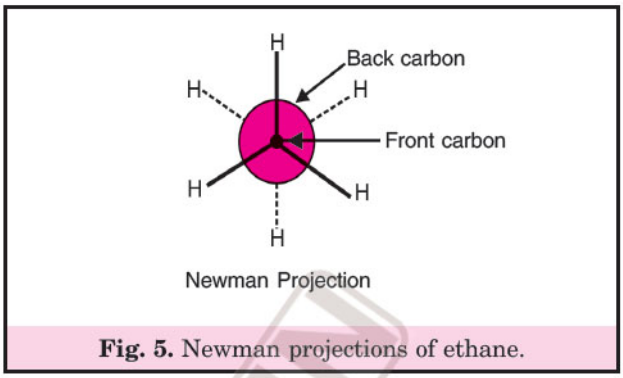

Fig. 5. Newman projections of ethane.

Let us understand the conformations of ethane. Out of all the conformations for ethane, only two extreme conformations are important and these are :

1. *Staggered conformation* 2. *Eclipsed conformation*

1. Staggered conformation. *In this arrangement, the hydrogens of the two carbon atoms are staggered with respect to one another*. As a result, they are at maximum distance apart and have minimum repulsion between them.

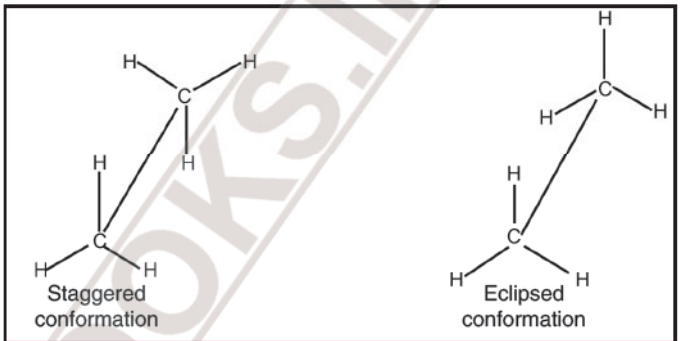

Fig. 6. Sawhorse representation of staggered and eclipsed conformations of ethane.

2. Eclipsed conformation. *In this conformation, the hydrogens of one carbon atom are directly behind those of the other.* Consequently, the repulsion in these atoms is maximum. The sawhorse projections of these conformations are represented in Fig. 6. The Newman projections for staggered and eclipsed conformations of ethane are shown in Fig. 7. It is clear that when the staggered conformation is rotated through an angle of 60°, it changes to eclipsed conformation and similarly, when eclipsed conformation is rotated through the same angle, it gives back the staggered conformation.

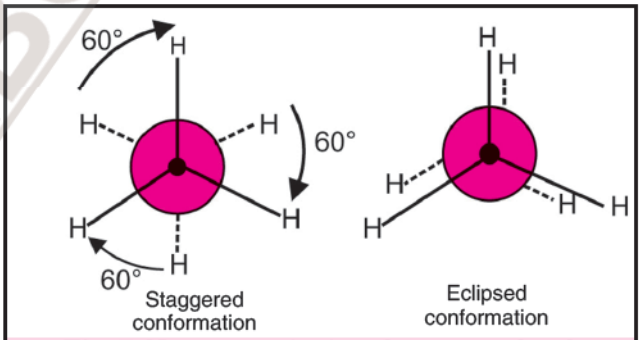

Fig. 7. Newman projections for staggered and eclipsed conformations of ethane.

Relative Stabilities of the Conformations of Ethane

The two conformations of ethane differ in their relative stabilities. In staggered conformation of ethane, the electron clouds of carbon–hydrogen bonds are as far apart as possible and therefore, the staggered conformation has minimum repulsions between the H-atoms attached tetrahedrally to the two carbon atoms. On the other hand, in the eclipsed conformation the electron clouds of the carbon–hydrogen bonds are closer to each other and therefore, eclipsed conformation has maximum force of repulsion between H-atoms. Therefore, the staggered conformation is more stable than the eclipsed conformation. So, when the staggered form changes into the eclipsed form, the repulsion forces increase and the molecule will possess more energy and thus loses stability. These repulsive interactions between the electron clouds which affect the stability of a conformation is called **torsional strain**. The magnitude of torsional strain depends upon the angle of rotation about C–C bond. This angle is also called **dihedral angle** or **torsional angle**. Thus, of the conformations of ethane, the staggered form

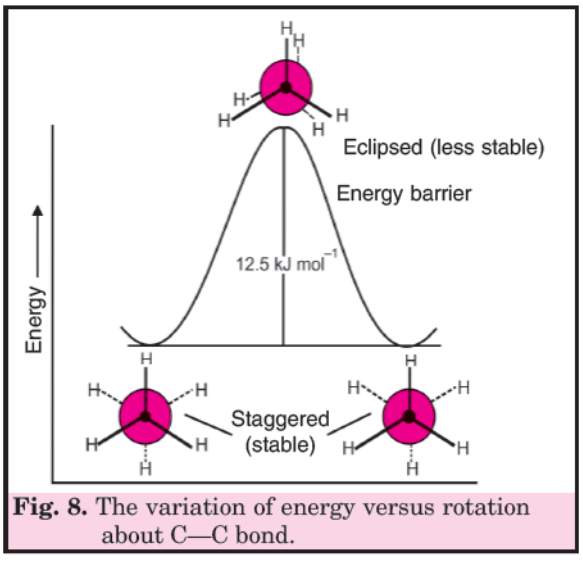

Fig. 8. The variation of energy versus rotation about C—C bond.

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has the least torsional strain while eclipsed form has maximum torsional strain. Thus, the rotation around C–C bond in ethane is completely free. The difference in the energy contents of the staggered and eclipsed conformations is 12.5 kJ mol^{-1}. This small barrier to rotation is also called **torsional barrier** of the single bond. However, *this energy difference is not large enough to prevent rotation.* Even at ordinary temperatures, the molecules have thermal or kinetic energy to overcome this energy barrier. Therefore, *the two conformations of ethane go on changing from one form to another and consequently, it is not possible to isolate the different conformations of ethane.*

The variation of energy versus rotation about the C—C bond has been shown in Fig. 8.

The difference in the energy of various conformations constitutes an **energy barrier to rotation.**

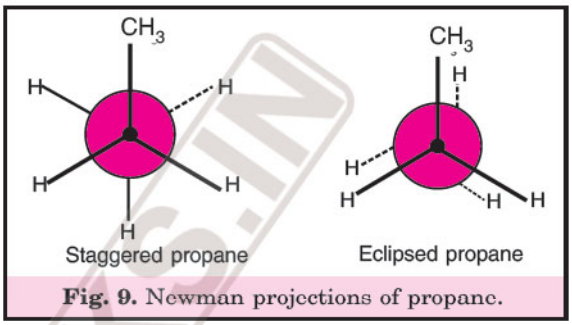

Fig. 9. Newman projections of propane.

Conformations of Propane *

The next higher member in alkane series, propane ($CH_3CH_2CH_3$) has also two extreme conformations : **staggered conformation** and **eclipsed conformation.** In. Fig. 9, only Newman projections are shown for simplicity. However, the energy barrier in propane is 14 kJ mol^{-1}, which is slightly higher than that in ethane.

In the eclipsed confirmation of propane, there are two ethane type H–H interactions and an additional interaction between C–H bond and C–C bond (of methyl group). The variation of energy versus rotation about C–C bond as shown in Fig. 10.

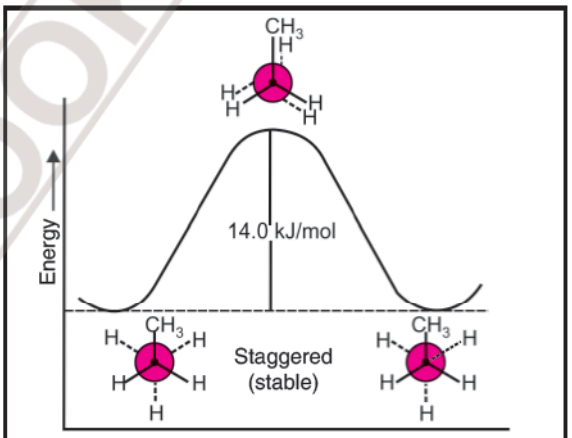

Fig. 10. The variation of energy versus rotation about C–C bond in propane.

Conformations of Butane*

As the alkane molecule becomes larger, the conformation situation becomes more complex. In butane ($CH_3CH_2CH_2CH_3$), for example, the rotation about the single bond between two inner carbon atoms (C_2 and C_3) is considered. In this case, all the staggered as well as eclipsed conformations will not have same stability and energy because of different types of interaction between C–C (of methyl) and C–H bonds. The lowest energy conformation will be the one, in which the two methyl groups are as far apart as possible *i.e.*, 180° away from each other.

This conformation will be maximum staggered and is called **anti conformation** (marked I). Other conformations can be obtained by rotating one of the C_2 or C_3 carbon atoms through an angle of 60° as shown ahead.

As is clear from the above Newman projections, the **Gauche or Skew conformations** (III and V) are also staggered. However, in these conformations, the methyl groups are so close that they repel each other. This repulsion causes gauche conformations to have about 3.8 kJ mol^{-1} more energy than anti conformation. The conformations II and VI are **eclipsed conformations.** These are unstable because of repulsions. These are 16 kJ mol^{-1} less stable than anti conformation. Conformation IV is also eclipsed and it is least stable having energy 19 kJ mol^{-1} more than anti conformation. This is because of repulsion between methyl-methyl groups which are very close together. It is called **fully eclipsed conformation.**

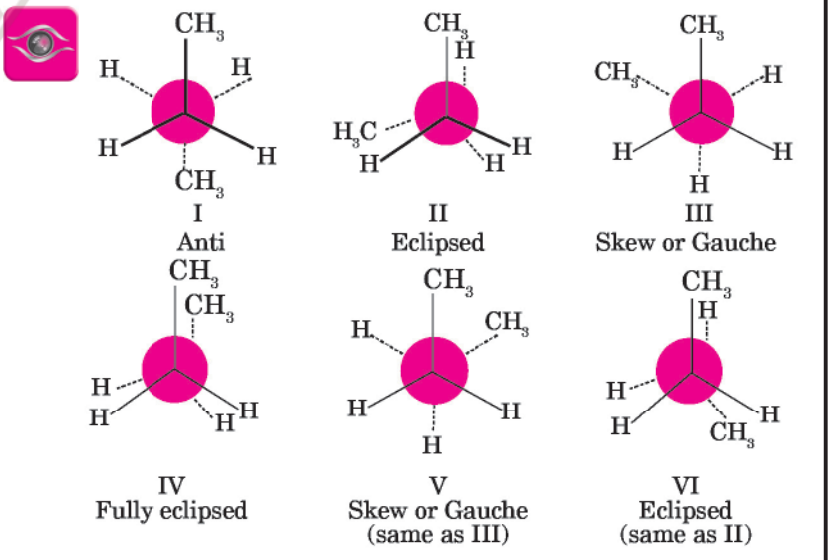

Fig. 11. Different conformations of butane

* Conformations of propane and butane are not in CBSE syllabus. These are discussed for competitive examinations.

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The **order of stability** of these conformations is :

Anti > Skew or Gauche > Eclipsed > Fully eclipsed.

The energy differences between various conformations is shown below :

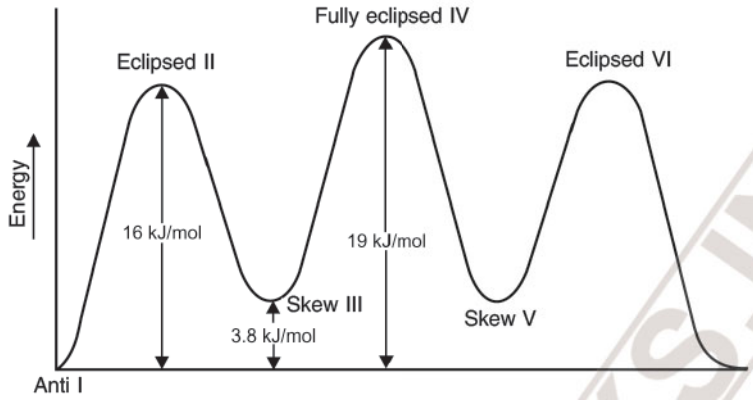


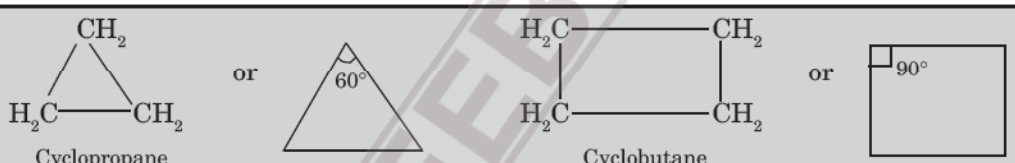
Fig. 12. Energy changes during rotation about C_2–C_3 bond of *n*-butane :

$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

LEARNING PLUS

Conformations in Cycloalkanes

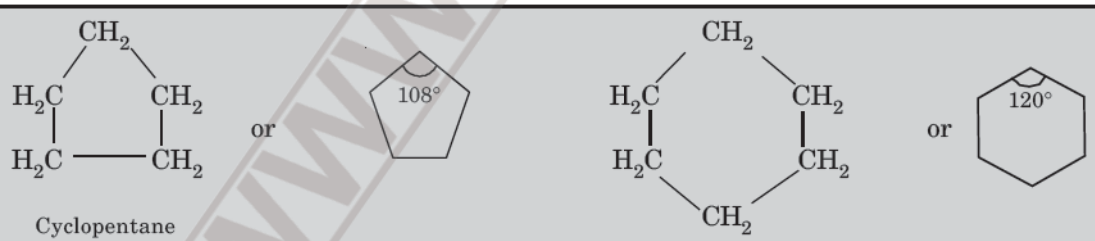
Conformational isomerism has also been observed in cycloalkane molecules. Cyclopropane and cyclobutane are planar molecules having bond angles of 60° and 90° respectively.



Cyclopropane
Bond angle = 60°

Cyclobutane
Bond angle = 90°

The bond angles in these molecules are quite different from the normal tetrahedral bond angle of 109.5°, which is a normal angle for sp^3 hybridised carbon atoms. As a result of deviation from normal bond angle, there is a considerable *strain* in the molecules of these compounds. Therefore, these are quite reactive. Obviously, cyclopropane with a bond angle of 60° is more strained and reactive than cyclobutane (bond angle 90°).



Cyclopentane
Bond angle 108°

Cyclohexane
Bond angle 120°

In cyclopentane, the bond angle is 108° which is quite close to normal tetrahedral angle. Therefore, cyclopentane has very less strain and is, therefore, stable. Similarly, the bond angle in cyclohexane ring is 120° and is expected to be quite reactive and strained. However, *cyclohexane is quite stable.* The stability of cyclohexane indicates that the molecule avoids strain by assuming conformation in which all the bond angles between carbon atoms are close to tetrahedral angle of 109.5°. Therefore, cyclohexane adopts a *non-planar structure.* Herman Sachoe proposed two important conformations for cyclohexane based on the fact that the molecule is *non–planar* or *puckered.* These important conformations for cyclohexane are the **chair form** and the **boat form** as shown in Fig. 13. In these structures, the tetrahedral angle is almost retained and the molecule is free from any angle strain. These structures are also called **puckered ring structures.** The names of these forms are due to resemblance of their shapes with chair and boat respectively.

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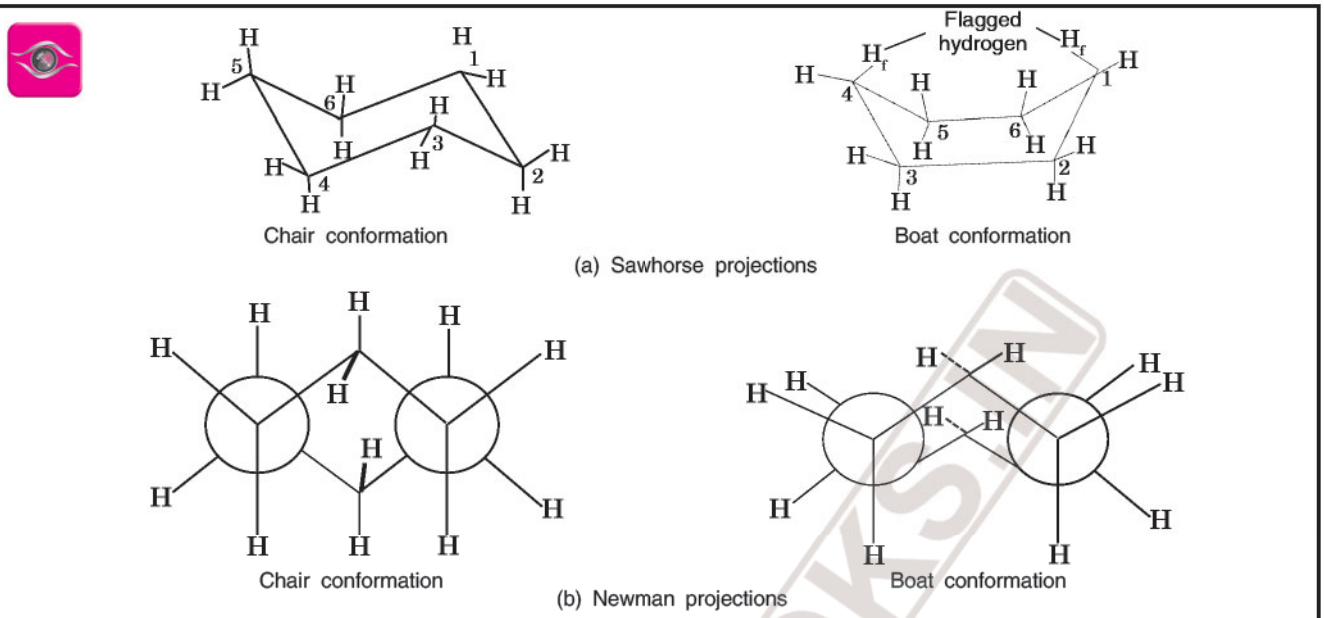


Fig. 13. Chair and boat conformations of cyclohexane.

Stabilities of the conformations of cyclohexane. The chair conformation of cyclohexane is more stable than the boat conformation due to the following reasons :

(*i*) In chair conformation, the adjacent hydrogen atoms on all the neighbouring carbon atoms are quite staggered and the force of repulsion in them is the minimum. However, in the boat conformation, the adjacent hydrogen atoms on C_2—C_3 and C_5—C_6 atoms are eclipsed.

(*ii*) The two hydrogen atoms (marked as H_f) bonded to the C_1 and C_4 atoms in boat conformation are quite close (distance = 183 pm) and repel each other. These are called ***flag pole hydrogens.*** Therefore, the energy of the boat conformation is more than that of chair conformation.

The energy of the boat conformation of cyclohexane is about 44 kJ mol^{-1} more than that of chair conformation. Therefore, *cyclohexane exists mainly in the chair form.*

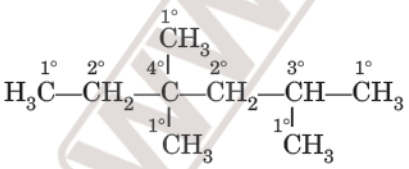
Thus, cyclopropane is planar, cyclobutane is almost planar while cyclopentane and cyclohexane are non-planar.

SOLVED EXAMPLES

❑ **Example 6.**

In the alkane H_3C—CH_2—$C(CH_3)_2$—CH_2—$CH(CH_3)_2$, identify 1°, 2° and 3° carbon atoms and give the number of H atoms bonded to each one of these.

Solution: 1°, 2° and 3° carbon atoms are labelled as : *N.C.E.R.T.*



No. of H atoms bonded to each C atom :
1° = 3H, 2° = 2H, 3° = 1H and 4° = No H

❑ **Example 7.**

Which of the following has the highest boiling point ?

(i) 2-Methylpentane (ii) 2, 3-Dimethylbutane (iii) 2, 2-Dimethylbutane

Solution: 2-Methylpentane has highest boiling point because it has the least branched chain structure as compared to 2,3-Dimethylbutane and 2, 2-Dimethylbutane. Therefore, it has largest surface area and, hence has the highest boiling point.

❑ **Example 8.**

Sodium salt of which acid will be needed for the preparation of propane ? Write chemical equation for the reaction. *N.C.E.R.T.*

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Solution:

Sodium salt of butanoic acid is needed for the preparation of propane.

$$CH_3CH_2CH_2COO^-Na^+ + NaOH \xrightarrow{CaO} \underset{\text{Propane}}{CH_3CH_2CH_3} + Na_2CO_3$$

❑ **Example 9.**

Complete the reactions

(i) $CH_3CH_3 + HNO_3 \xrightarrow{vapour\ phase}$

(ii) $CH_4 + O_2 \xrightarrow[723\text{-}773\ K]{Copper\ tube}$

(iii) $C_2H_5COONa + NaOH \xrightarrow{CaO}$

Solution: *(i)* $CH_3CH_3 + HNO_3 \xrightarrow{\text{vapour phase}} \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2} + H_2O$

(ii) $CH_4 + O_2 \xrightarrow[723 - 773\ K]{\text{Copper tube}} \underset{\text{Methanol}}{2CH_3OH}$

(iii) $C_2H_5COONa + NaOH \xrightarrow{CaO} \underset{\text{Ethane}}{C_2H_6} + Na_2CO_3$

Practice Problems

- **3.** Name the two extreme type of conformations of ethane.
- **4.** Arrange the different type of conformations of butane in the decreasing order of stability.
- **5.** Out of boat and chair form of cyclohexane, which is more stable ?
- **6.** Does the eclipsed conformation of propane has same energy or different as eclipsed conformation of ethane ?
- **7.** Arrange the following in the decreasing order of boiling points :
  (i) *n*-Pentane *(ii)* Iso-pentane *(iii)* Neo-pentane
- **8.** Arrange the following alkanes in the increasing order of their melting points :
  (i) *n*-C_4H_{10} *(ii)* *n*-C_5H_{12} *(iii)* *n*-C_3H_8 *(iv)* *n*-C_6H_{14}
- **9.** Name the products which may be obtained when a mixture of methyl bromide and ethyl bromide is treated with sodium metal in ether.
- **10.** Which salt on treatment with soda lime gives ethane ?
- **11.** Name the product obtained by heating butanoic acid with sodalime at 630 K. Name any other acid which also gives the same product under similar conditions.
- **12.** Draw the structures of the following showing all C and H atoms :
  (i) 2-Methyl-3-isopropyl heptane
  (ii) Dicyclopropyl methane

Answers to Practice Problems

- **3.** Staggered, eclipsed
- **4.** Anti > Skew > Eclipsed > Fully eclipsed
- **5.** Chair form is more stable.
- **6.** Different energy. Eclipsed conformation of ethane is more stable than that of propane.
- **7.** *(i)* > *(ii)* > *(iii)*
- **8.** *(iii)* < *(i)* < *(ii)* < *(iv)*
- **9.** Ethane, propane and butane.
- **10.** Sodium propanoate.
- **11.** $\underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH} + 2NaOH \xrightarrow{CaO} \underset{\text{Propane}}{CH_3CH_2CH_3} + Na_2CO_3 + H_2O.$

  2-Methylpentanoic acid also gives the same product (propane).

  $\underset{\text{2-Methylpropanoic acid}}{(CH_3)_2CHCOOH} + 2NaOH \xrightarrow{CaO} \underset{\text{Propane}}{CH_3CH_2CH_3} + Na_2CO_3 + H_2O.$

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CHEMISTRY OF ALKENES

Alkenes are unsaturated hydrocarbons containing carbon–carbon double bond (C=C) in their molecules. **They have the general formula C_nH_{2n}. The simplest member of the alkene family is ethene, C_2H_4.** The alkenes are also called **olefins** (Greek *olefiant* meaning oil forming) because the larger members of the series (such as ethylene, propylene, etc.) react with chlorine to form oily products.

STRUCTURE OF DOUBLE BOND

Carbon–carbon double bond in alkenes consists of one sigma (σ) bond and one pi (π) bond. For example, in the formation of ethene, one sp^2 hybridised orbital of carbon overlaps axially (head on) with the similar sp^2 hybrid orbital of other carbon atom to form a stable σ bond. On the other hand, the unhybridized $2p_z$ orbitals of two carbon atoms overlap sidewise to form π bond. Each of the remaining two sp^2 hybrid orbitals of each carbon atom overlaps axially with the half filled 1*s* orbital of hydrogen to form σ bonds as shown in Fig. 14.

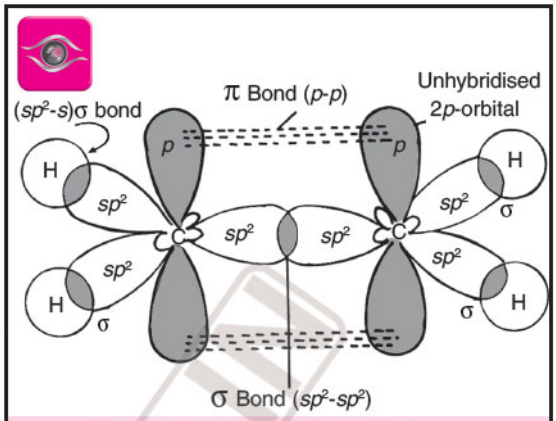


Fig. 14. Orbital picture of ethene.

Electron diffraction studies have shown that ethene is a flat molecule *i.e.*, all the bonds in the molecule lie in a plane. The H—C—H bond angle is 116.6° and C—C—H bond angle is 121.7° (Fig. 15). The values of the bond angles are quite close to the values for sp^2 hybridised molecules. The values of the bond lengths for C — H and C ═C bonds are 110 pm and 134 pm respectively.

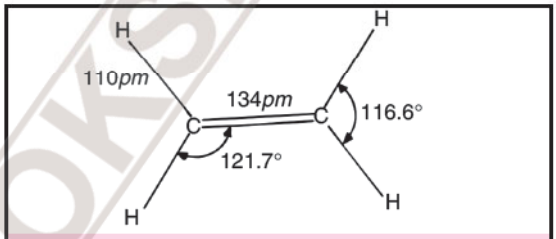


Fig. 15. Bond angles and bond lenths in ethylene.

It may be pointed out that the carbon-carbon bond length in ethane molecule is 154 pm whereas that in ethene molecule is 134 pm. This means that C═C bond is shorter than C—C bond. This can be explained on the basis of extent of overlapping of orbitals. Carbon—carbon double bond involves the formation a σ bond and a π-bond. For the formation of π-bond the bonding orbitals have to come close together which shortens the distance between the constituent atoms. Moreover, the effective size of sp^2 hybrid orbitals is smaller than sp^3 hybrid orbitals. This also decreases the distance between the constituent carbon atoms in ethene molecule.

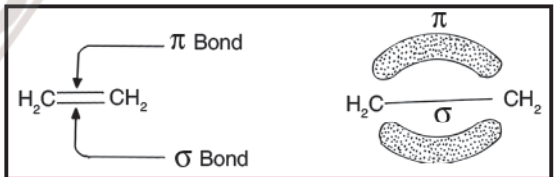


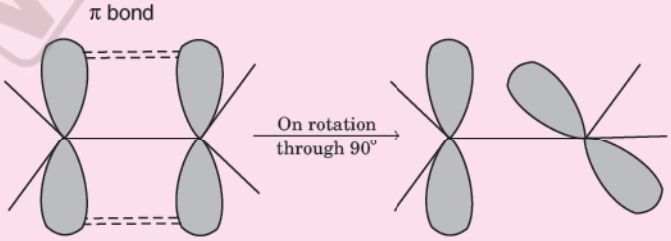
Fig. 16. Representation of double bond.

Nature of the double bond

The C == C bond often known as ethylenic double bond, is made up of a sigma (σ) bond and a pi (π) bond (Fig. 16). The sigma bond is a strong bond having bond dissociation enthalpy of about 397 kJ mol^{-1} while pi bond is a weak bond having bond dissociation enthalpy of about 284 kJ mol^{-1}. This is because σ-bond is formed by head on overlapping of orbitals while the π-bond is formed by lateral or sidewise overlapping of the orbitals. Since extent of overlapping is less in case of π-bond than σ-bond, therefore, a π-bond is weaker bond than a σ-bond. Due to the presence of weak π-bond, alkenes are highly reactive molecules and have a tendency to take part in chemical reactions. Strength of the double bond (bond enthalpy 681 kJ mol^{-1}) is greater than that of a carbon-carbon single bond in ethane (bond enthalpy 348 kJ mol^{-1}).

Geometrical Isomerism: Hindered rotation about the double bond.

From the orbital picture of ethene, it is evident that a double bond consists of a σ-bond and a π-bond. The two $2p_z$ orbitals participating in the π-bond are parallel to each other. The rotation of one carbon atom through 90° breaks the π-bond because in that case, the $2p_z$ orbitals become perpendicular to each other and no sidewise overlap is possible.



Lobes are perpendicular to each other
⟹ no overlap possible

But the breaking of π-bond requires 284 kJ mol^{-1} of energy which is not provided by the collisions of molecules at room temperature. Hence, ***the rotation about the double bond is restricted or hindered which leads to geometrical isomerism*** (discussed later).

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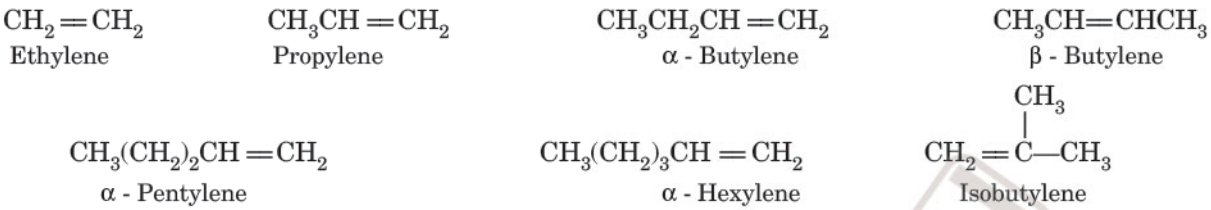
NOMENCLATURE OF ALKENES

Most alkenes are conveniently named by the IUPAC system. But common names are also sometimes used for simple compounds. These are already discussed in previous unit. Some of these are :



According to IUPAC system alkenes are named similar to alkanes with the following modifications :

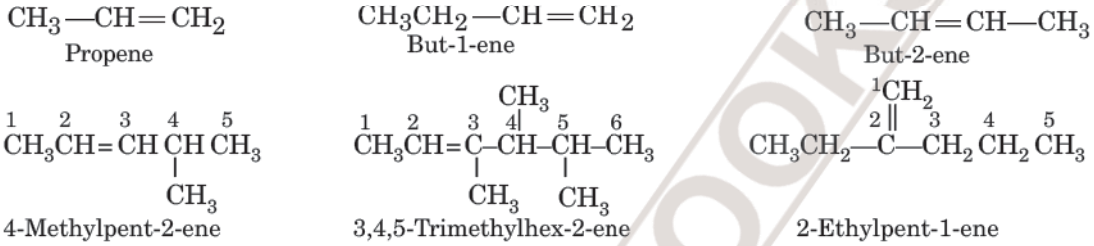
(i) The longest continuous chain should include both the carbon atoms of the double bond.

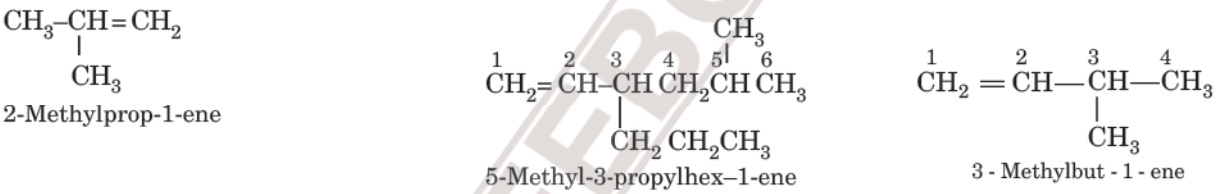
(ii) The suffix used for alkene is ***–ene.***

(iii) The chain is numbered from the end that gives the lower number to the first carbon atom of the double bond.

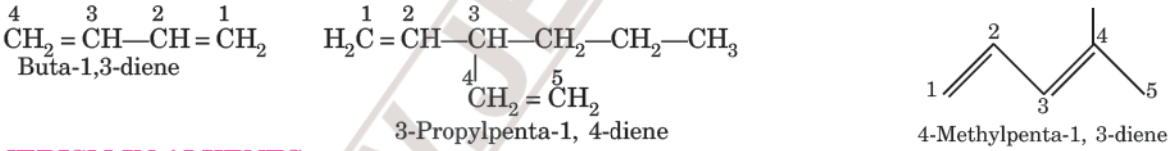
(iv) If there are two or more double bonds the ending ane of the alkane is replaced by ***adiene*** *or* ***atriene.***

For example,





The compounds containing two double bonds are named as dienes :



ISOMERISM IN ALKENES

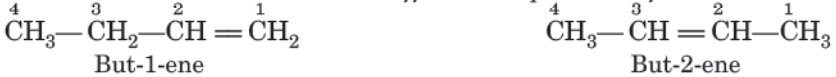
Alkenes exhibit the following isomerisms :

1. Structural isomerism

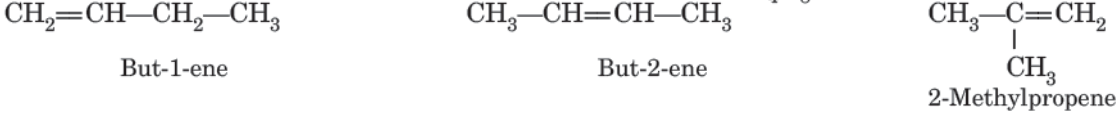
Alkenes show the following types of structural isomerisms :

(*i*) Chain isomerism. *The isomers differ with respect to the chain of carbon atoms.* As in alkanes, ethene (C_2H_4) and propene (C_3H_6) can have only one structure but alkenes higher than propene have different structures. For example, the alkene having molecular formula C_4H_8 exists as two chain isomers.

(*ii*) Position isomerism. *The isomers differ in the position of the double bonds.* For example,



Thus, there are three structural isomers for the molecular formula C_4H_8.



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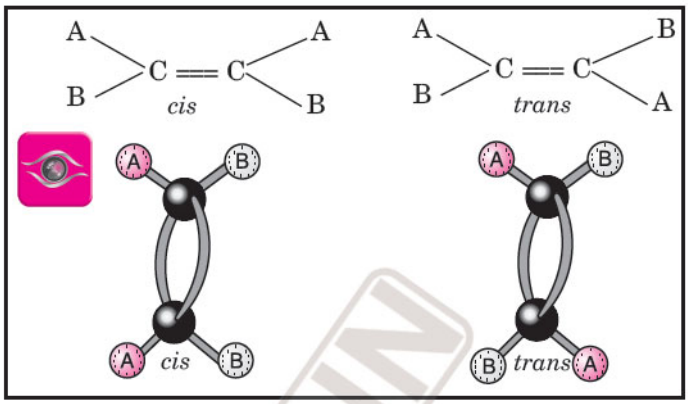
2. Geometrical isomerism

The geometrical isomerism is shown by alkenes. *The compounds which have the same structural formula but differ in the spatial arrangement of atoms or groups of atoms about the double bond* are called **geometrical isomers** and the phenomenon is known as **geometrical isomerism.** The geometrical isomerism is exhibited by certain members of the alkene family.



Cause of geometrical isomerism. We know that a double bond consists of a σ-bond and a π-bond. Due to the presence of π-bond, the groups or atoms attached to each sp^2-hybridised C-atom cannot rotate about it. They can do so only by breaking the π-electron cloud and require energy of the order of 284 kJ. Therefore, the rotation about the double bond is *restricted* or *hindered.* Because of the hindered rotation, the molecule of the type $C_2A_2B_2$ exhibits two space isomers which are also called **geometrical isomers.**

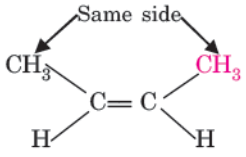
The isomer in which similar atoms or groups lie on the same side of the double bond is called ***cis*-isomer** while the other in which they are displaced on opposite sides, is called ***trans*-isomer.**

The geometrical isomerism is also called ***cis-trans* isomerism.**

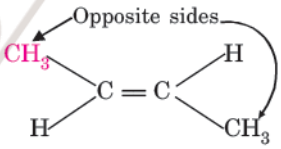
Conditions for geometrical isomerism. The main conditions for geometrical isomerism are :

1. *The molecule must have a double bond.*
2. *The two atoms or groups attached to the same carbon atom must be different.*

For example, but-2-ene ($CH_3CH = CHCH_3$) exhibits geometrical isomerism.

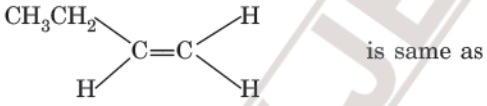


cis-But-2-ene



trans-But-2-ene

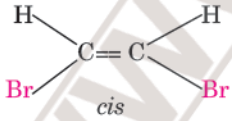
But its position isomer but-1-ene ($CH_3CH_2CH = CH_2$) does not show geometrical isomerism because the two same hydrogen atoms are attached to the double bonded carbon atom.



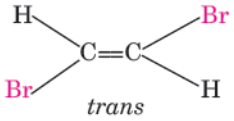
Not geometrical isomers

Other examples are :

(*i*) 1, 2-Dibromoethene

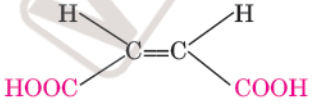


cis

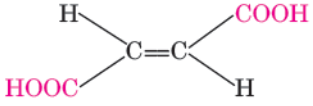


trans

(*ii*) Maleic acid and fumaric acid



Maleic acid (*cis*)



Fumaric acid (*trans*)

Geometrical or *cis* – *trans* isomerism is also shown by alkenes of the type XYC = CXZ and XYC = CZW.

Geometrical isomers have different physical properties. However their chemical properties are similar but not identical. These can be distinguished on the basis of many physical properties such as melting point, boiling point, solubility, dipole moment, refractive index, stability, etc. It may be noted, for example, that

(*i*) *Cis*-isomer is more polar than *trans*-isomer. For example, dipole moment of *cis*-dichloroethene is 1.90 D while that of the *trans*-form is almost zero. Similarly, dipole moment of *cis*-but-2-ene is 0.35 D while dipole moment of *trans*-but-2-ene is almost zero or it can be said that *trans*-but-2-ene is nonpolar. This

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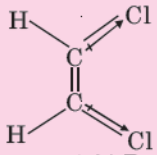
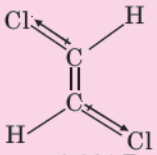
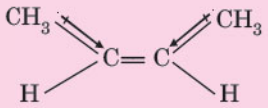
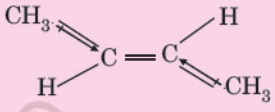
is clear from the figures that in *cis* form two bond polarities add up to give resultant polarity. But in case of *trans* alkenes, the bond polarity being in opposite directions cancel each other giving almost zero polarity of the molecules.

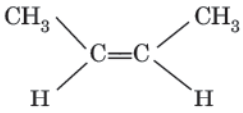

μ = 1.90 D
(*cis*)

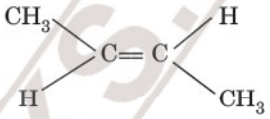

μ = 0.001 D
(*trans*)


μ = 0.33D
cis–But-2-ene


μ = 0 D
trans–But-2-ene

(*ii*) *Cis*-isomer has higher boiling point than *trans*-isomer :


cis-But-2-ene
(b.p. = 277K)


trans–But-2-ene
(b.p. = 274K)

(*iii*) In case of solids, the *trans*- isomer has higher melting point than *cis*-isomer. This may be attributed to better symmetry of the *trans* isomer due to which the *trans* solids fit very well into the crystal lattice. Therefore, *trans* isomers have high melting points.

(*iv*) *Cis*-isomer has higher refractive index than *trans*-isomer.

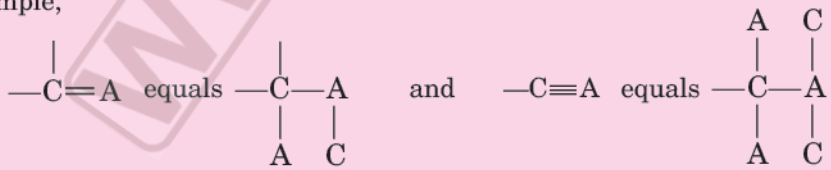
(*v*) The stability of *trans*-isomer is more than *cis*-isomer.

E, Z-System for Geometrical Isomers

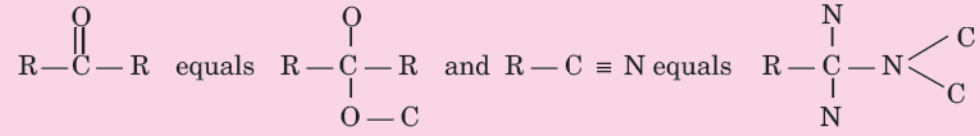
When there are three or four different groups attached to the carbon atoms of a double bond, it becomes difficult to assign *cis* and *trans* designation to isomers. To overcome this problem, a more general system of geometrical isomers called the **E** and **Z system** was devised.

The **E** and **Z** system is based on the assignment of priorities to the atoms or groups attached to each carbon of the double bond. The priorities can be assigned on the basis of the rules given by Cahn-Ingold and Prelog. The rules are :

1. *If the four atoms attached to the double bonded carbon atoms are different, priority depends on the atomic number.* The atom with higher atomic number gets highest priority. For example, if the four atoms attached are F, Cl, Br and I, the priority becomes :
   $$I > Br > Cl > F$$
2. *If two isotopes of the same element are present, the isotope of higher mass number gets the higher priority.* For example, deuterium (D) gets priority over hydrogen (H).
3. *If two atoms are identical, the atomic numbers of the next atoms are considered for priority assignment.* For example, if CH_3 and C_2H_5 are attached, C_2H_5 gets priority because atoms attached to first C atom are C, H and H whereas in CH_3 group, atoms attached are H, H and H only.
4. *Where there is a double bond or triple bond, both atoms are considered to be duplicated or triplicated.* For example,



e.g.,



E, Z-system. *If the two higher priority groups are on the same side of the double bond, the isomer is called* **Z** *(German, Zusammen meaning together) and if the two higher priority groups are on the opposite side of the double bond, the isomer is called* **E** (German, *entgegen* meaning opposite).

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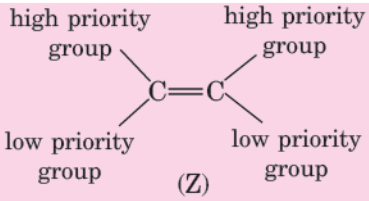
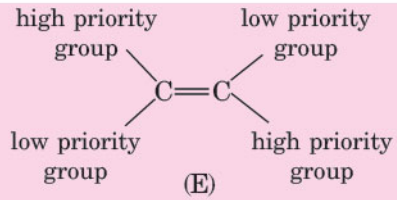


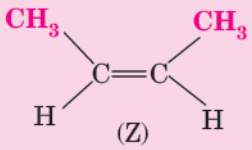
(Z)

(high priority groups on the same side)

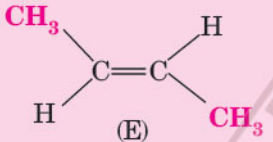


(E)

(high priority groups on the opposite side)



(Z)

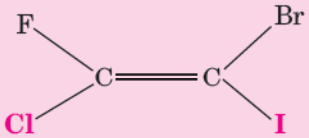


(E)

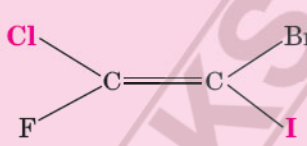
(Priority $CH_3 > H$)

The atoms or groups of higher priority are shown bold coloured.

For example,

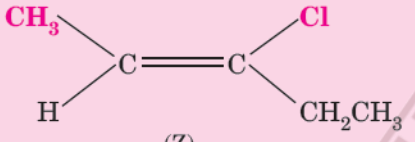


(Z)

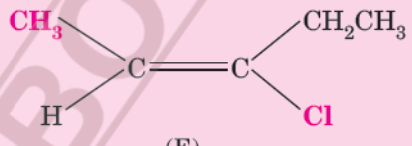


(E)

(Priority : Cl > F and I > Br)

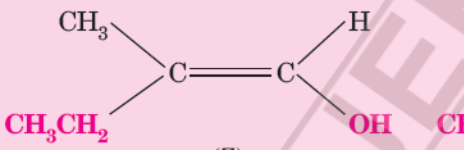


(Z)

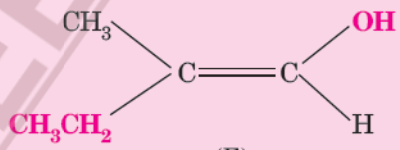


(E)

(Priority : CH_3 > H and Cl > CH_2CH_3)



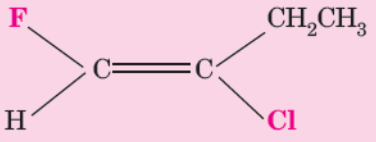
(Z)



(E)

(Priority : $C_2H_5 > CH_3$ and OH > H)

(Z)



(E)

(Priority : F > H and Cl > C_2H_5)

SOLVED EXAMPLES

Example 10.

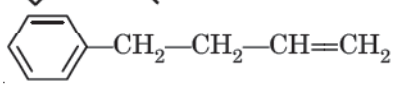
Write IUPAC names of the following compounds :

(i) $CH_3CH{=}C(CH_3)_2$

(ii)

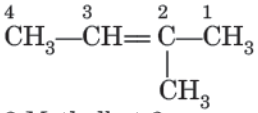
(iii) $CH_3{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH_2$

(iv)



Solution:

(i)



2-Methylbut-2-ene

(ii) $CH_2{=}CH{-}CH{=}CH_2$

Penta-2, 4-diene

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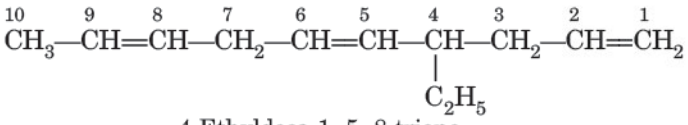
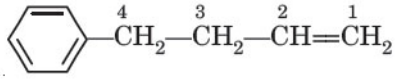
(iii) 

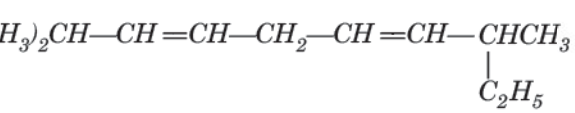
4-Ethyldeca-1, 5, 8-triene

(iv) 

4-Phenylbut-1-ene

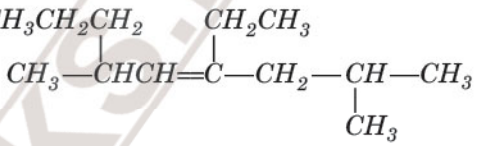
❑ Example 11.

Write IUPAC names of the following compounds and calculate the number of sigma and pi bonds in these

(i) 

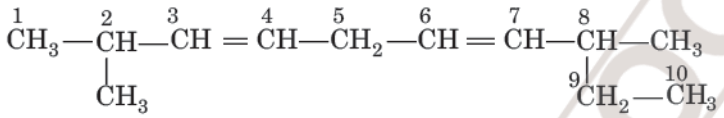
(ii)

(iii) $CH_2{=}C(CH_2CH_2CH_3)_2$

(iv) 

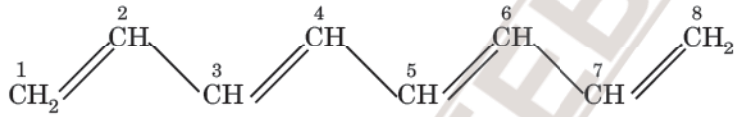
N.C.E.R.T.

Solution:

(i) 

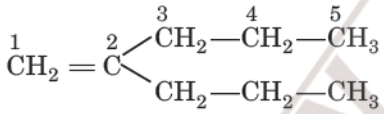
2,8-Dimethyldeca-3,6-diene

σ-bonds = 33, π-bonds = 2

(ii) 

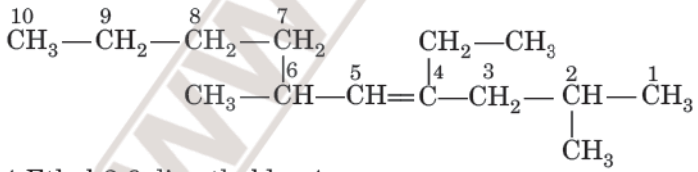
Octa-1,3,5,7-tetraene

σ-bonds = 17, π-bonds = 4

(iii) 

2-Propylpent-1-ene

σ-bonds = 23, π-bond = 1

(iv) 

4-Ethyl-2,6-dimethyldec-4-ene

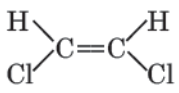
σ-bonds = 41, π-bond = 1

❑ Example 12.

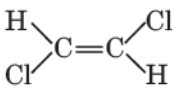
Draw cis and trans isomers of the following compounds and write their IUPAC names

(a) $CHCl = CHCl$ (ii) $C_2H_5C(CH_3) = C(CH_3)C_2H_5$ **N.C.E.R.T.**

Solution:



cis-1,2-Dichloroethene



trans-1,2-Dichloroethene

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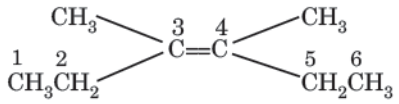
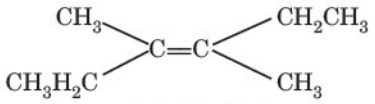


cis-3,4,-Dimethylhex-3-ene

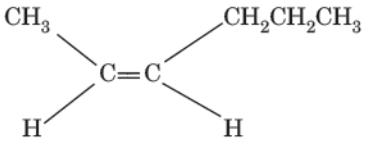


trans-3,4,-Dimethylhex-3-ene

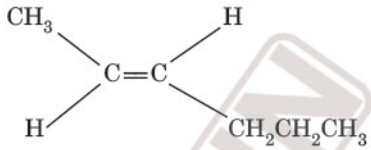
Example 13.

Draw cis and trans isomers of hex-2-ene. Which isomers will have higher boiling point and why ?

Solution:



cis- Hex-2-ene



trans-Hex-2-ene

The *cis* form will have higher boiling point due to more polar nature of the molecule leading to strong intermolecular dipole-dipole interactions. As a result of stronger intermolecular interactions it requires more energy to separate the molecules.

Example 14.

Write the structures and IUPAC names of different structural isomers of alkenes corresponding to the molecular formula C_5H_{10}. **N.C.E.R.T.**

Solution:

(*a*) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$: Pent-1-ene

(*b*) $\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}-\overset{5}{CH_3}$: Pent-2-ene

(*c*) $CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_2-CH_3$: 2-Methylbut-1-ene

(*d*) $\overset{1}{CH_2}=\overset{2}{CH}-\underset{\displaystyle CH_3}{\overset{\displaystyle 3}{\overset{\displaystyle |}{CH}}}-\overset{4}{CH_3}$: 3-Methylbut-1-ene

(*e*) $\overset{1}{CH_3}-\underset{\displaystyle CH_3}{\overset{\displaystyle 2}{\overset{\displaystyle |}{C}}}=\overset{3}{CH}-\overset{4}{CH_3}$: 2-Methylbut-2-ene

Example 15.

Which of the following compounds will show geometrical isomerism ?

(*a*) $H_2C=CBr_2$ (*b*) $(H_3C)_2C=CHCH_3$ (*c*) $C_6H_5CH=CHCH_3$

(*d*) $CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CHCH_2CH_3$ (*e*) $H_3C-CH=CCl(CH_3)$

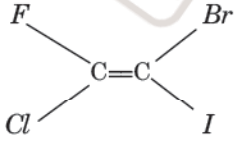
N.C.E.R.T.

Solution: (*c*), (*d*) and (*e*) show geometrical isomerism.

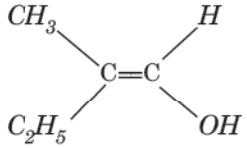
Example 16.

Classify the following as Z or E isomers :

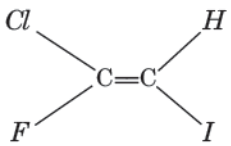
(*a*)



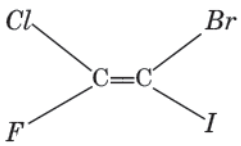
(*b*)



(*c*)



(*d*)



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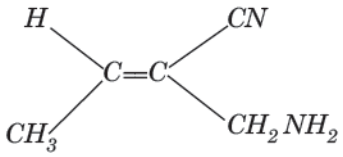
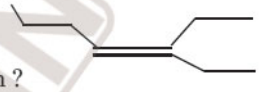
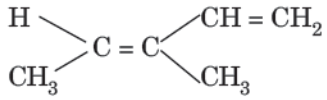
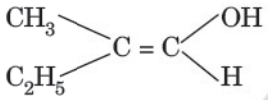
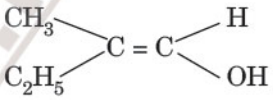
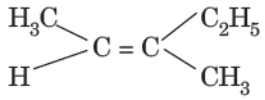
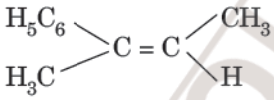
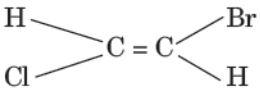
(e) 

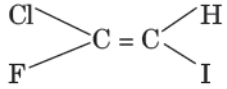
Solution: (a) Z (b) Z (c) E (d) E (e) E

Practice Problems

13. Which of the following molecules can exhibit geometrical isomerism ?
(i) 2-Methylbut-2-en-1-ol (ii) 3-Methylbut-2-en-1-ol (iii) 

14. Which of the following alkene does not have E configuration according to E, Z system ?
(i)  (ii)  (iii) 

15. Classify the following as E or Z isomers :
(i)  (ii)  (iii) 

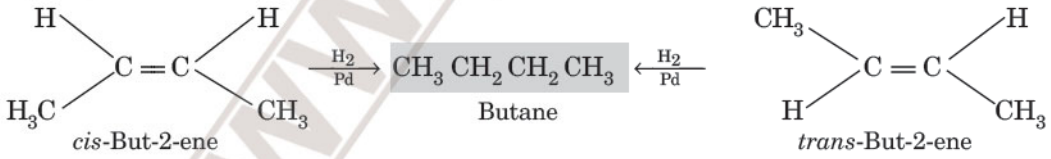
(iv) 

Answers to Practice Problems

13. (i)
14. (iii)
15. (i) Z (ii) Z (iii) E (iv) E

STABILITY OF ALKENES

The relative stability of alkenes can be determined by comparing their enthalpies of hydrogenation. **Enthalpy of hydrogenation *is the heat evolved when one mole of alkene reacts with hydrogen.*** For example, both the geometrical isomers of but–2–ene consume one mole of H_2 and produce the same product, butane upon catalytic hydrogenation in the presence of a catalyst such as platinum or palladium.



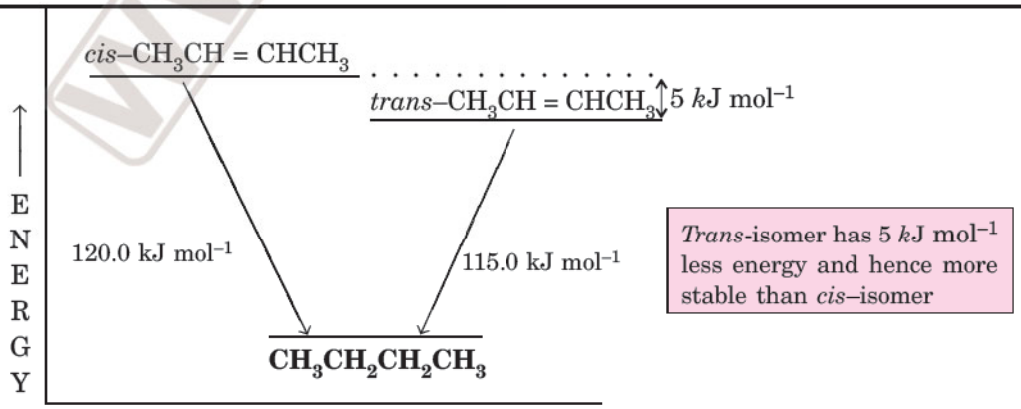


Fig. 17. Enthalpies of hydrogenation and stability of *cis*- and *trans* but-2-ene.

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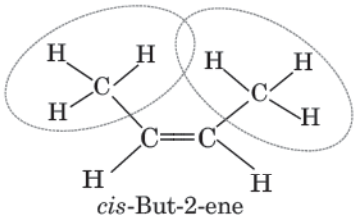
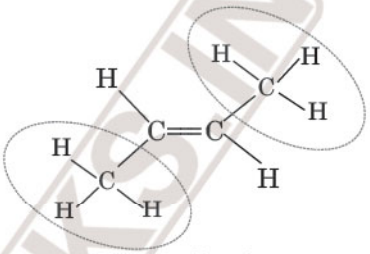
It has been observed that enthalpy of hydrogenation of *cis*-isomer is 120.0 kJ mol^{-1} and that of *trans*-isomer is 115.0 kJ mol^{-1}. Since the product has the same energy in both the reactions, any difference in the heat produced must be due to the difference in the energies of the starting alkene. The *trans*-isomer evolves about 5 kJ mol^{-1} less heat than the *cis*-isomer, it means that it contains 5 kJ mol^{-1} less energy. In other words, ***the trans-isomer is 5 kJ mol^{-1} more stable than the cis-isomer as shown in*** Fig. 17.

This is due to the fact that when large substituents are present on the same side of the double bond, as in a *cis*-isomer, their electron clouds can interact with each other resulting steric strain in the molecule. Because of steric strain, the molecule becomes less stable. On the other hand, when the large substituents are present on the opposite sides of the double bond, as in the *trans*-isomer, their electron clouds cannot interact and hence there is no destabilizing steric strain.

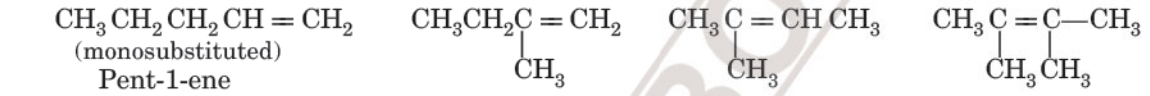


cis-But-2-ene
(steric strain)



trans-But-2-ene
(no steric strain)

Enthalpies of hydrogenation show that the stability of alkene also depends upon the position of double bond. For example, enthalpy of hydrogenation of some alkenes are given below :



(monosubstituted) Pent-1-ene — ΔH° = **–126 kJ mol^{-1}**

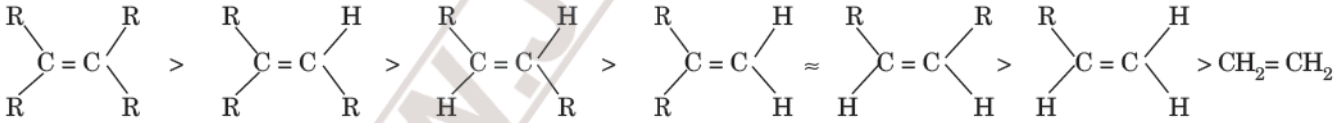
(disubstituted) 2-Methylbut-1-ene — ΔH° = **–119.5 kJ mol^{-1}**

(trisubstituted) 2-Methylbut-2-ene — ΔH° = **–112.5 kJ mol^{-1}**

(tetrasubstituted) 2, 3-Dimethylbut-2-ene — ΔH° = **–111.5 kJ mol^{-1}**

The above data indicate that the alkenes become more stable with increasing substitution. In other words, ***the greater the number of alkyl groups attached to the double bonded carbon atoms, the more stable is the alkene.***

Thus, the order of stability of alkenes is



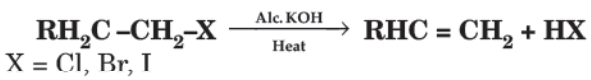
In general, the *trans*-isomer is slightly more stable than the corresponding *cis*-isomer.

PREPARATION AND PROPERTIES OF ALKENES

Preparation of Alkenes

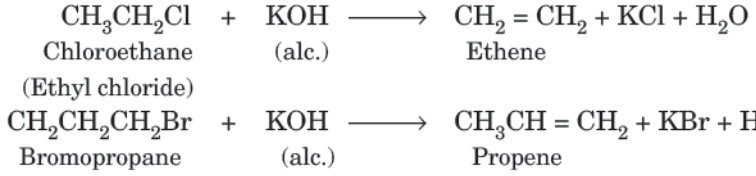
Alkenes can be prepared by the following methods :

1. From alkyl halides or haloalkanes. Alkenes can be prepared from alkyl halides (usually bromides or iodides) by heating with alcoholic potash (potassium hydroxide dissolved in ethanol). ***This reaction removes a molecule of halogen acid (HX) and therefore, the reaction*** is called ***dehydrohalogenation.***



X = Cl, Br, I

e.g.,



Chloroethane (Ethyl chloride) + KOH (alc.) → Ethene

Bromopropane (Propyl bromide) + KOH (alc.) → Propene

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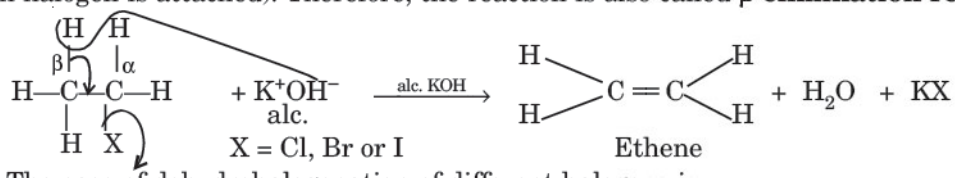
In this reaction, the hydrogen atom is eliminated from β carbon atom (carbon atom next to the carbon to which halogen is attached). Therefore, the reaction is also called **β-elimination reaction.**

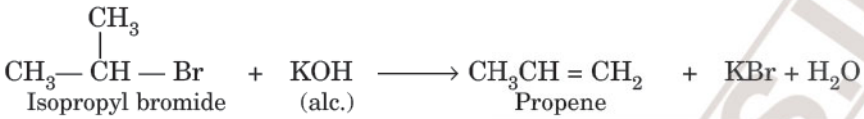


The ease of dehydrohalogenation of different halogens is :

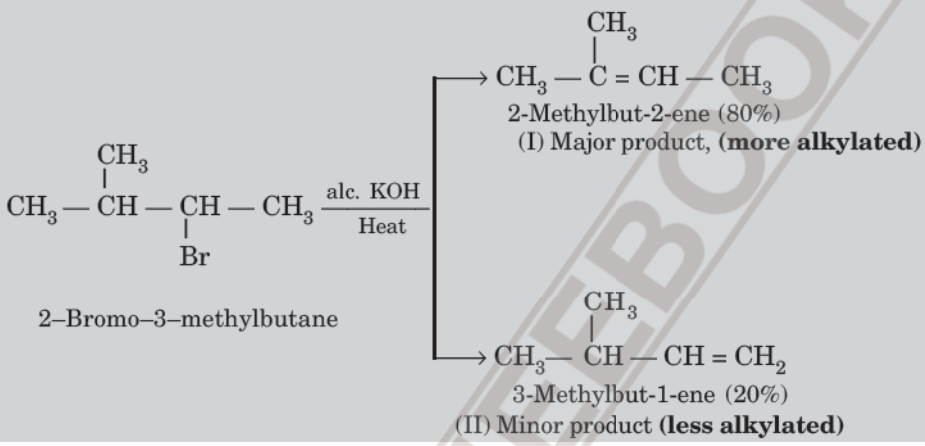
Iodine > Bromine > Chlorine

For alkyl groups, the ease of reaction is :

Tertiary > Secondary > Primary

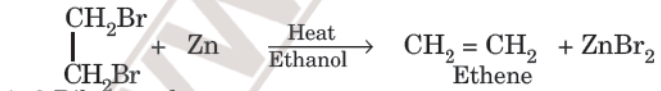


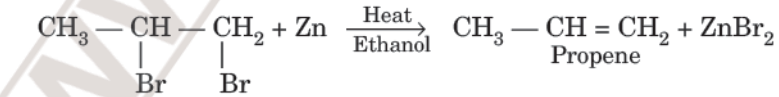
In case the alkyl halide can undergo dehydrohalogenation in two different ways, *that alkene is preferred which is more alkylated, i.e.* have more number of alkyl groups attached to double bonded carbon atoms. This is known as **Saytzeff rule.** For example,



The alkene (I) is trialkylated and alkene (II) is monoalkylated. Therefore, alkene (I) is the major product.

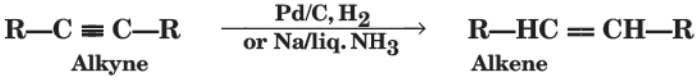
2. From dihalogen derivatives (vicinal dihalides). Dihalogen derivatives of alkanes in which two halogen atoms are attached to adjacent carbon atoms (called **vicinal dihalogen derivatives)** are converted to alkenes by heating with zinc dust in ethanol. For example,



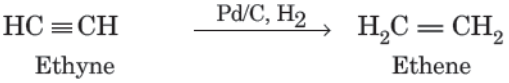


This ***reaction of removal of halogen (Cl₂, Br₂ or I₂) from a dihaloalkane to form an alkene*** is called ***dehalogenation reaction.***

3. From alkynes. Alkynes can be reduced to alkenes using palladium-charcoal (palladised charcoal) catalyst partially deactivated with poison like sulphur compounds or quinoline. Partially deactivated palladised charcoal is known as **Lindlar's catalyst.** Alkynes can also be reduced to alkenes with sodium in liquid ammonia (called **Birch reduction**).



e.g.,



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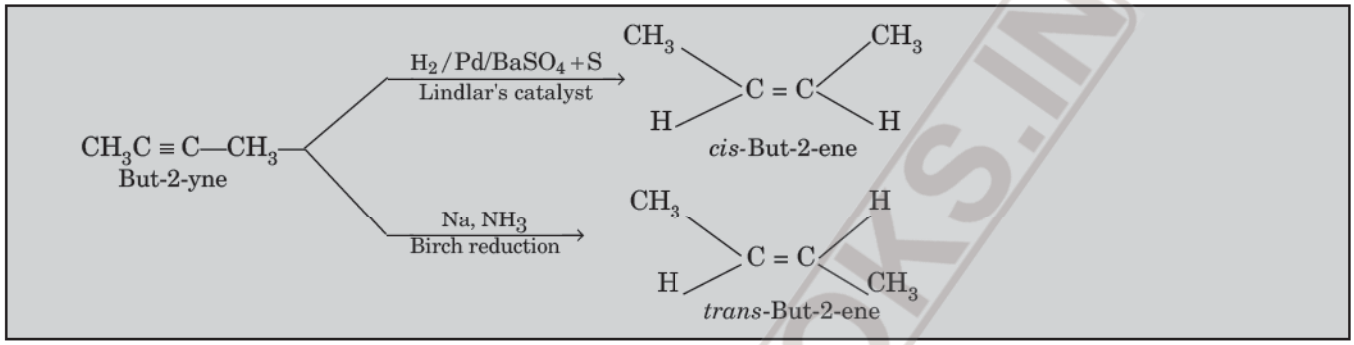
$$CH_3C \equiv CH + H_2 \xrightarrow[or\ Na/liq.\ NH_3]{Pd/C,\ H_2} CH_3CH = CH_2$$
Propyne — Propene

e.g.,
$$CH_3{-}C \equiv C{-}CH_3 \xrightarrow[or\ Na/liq.\ NH_3]{Pd/C,\ H_2} CH_3CH = CH\ CH_3$$
But-2-yne — But-2-ene

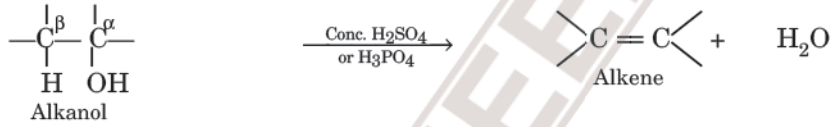
It may be noted that reduction of alkynes in presence of palladium supported over $BaSO_4$ or $CaCO_3$ and partially poisoned by S or quinoline (**Lindlar's catalyst**) gives predominantly ***cis* isomer.** However, if alkynes are reduced with lithium or sodium in liquid ammonia (***Birch reduction***) gives predominantly ***trans* alkene.**



4. From alcohols. Alkenes are prepared from alcohols by heating with protonic acids such as sulphuric acid or phosphoric acid at about 443 K. This reaction is called **dehydration of alcohols.**

$$CH_3CH_2OH \xrightarrow[443\ K]{H_2SO_4\ or\ H_3PO_4} CH_2 = CH_2 + H_2O$$
Ethyl alcohol — Ethene

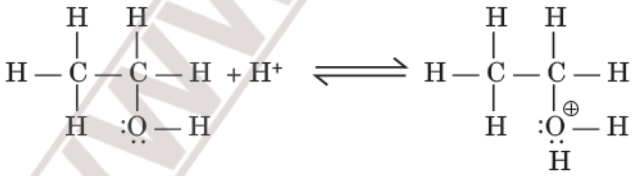
This reaction is also an example of β-elimination reaction because –OH group takes out one hydrogen atom from the β-carbon atom.



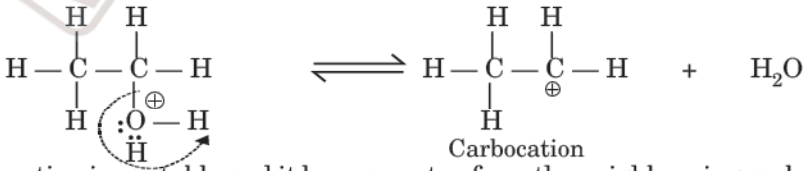
Mechanism :

The dehydration of alcohol occurs in the following steps :

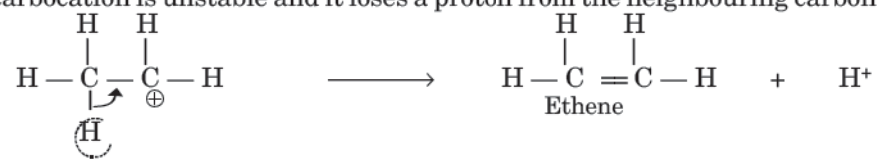
(*i*) *Alcohol gets protonated by the acid.* The proton from acid attacks the electron rich site of the alcohol and it gets attached to the O atom forming a protonated alcohol as :



(*ii*) Protonated alcohol loses a water molecule to give carbocation. This step is slow and hence is the rate determining step.



(*iii*) The carbocation is unstable and it loses a proton from the neighbouring carbon to form alkene (ethene).



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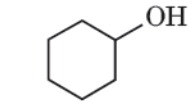
Similarly, propene is obtained by heating *n*-propyl alcohol with conc. H_2SO_4 at 443 K.

$$\underset{\text{n-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow[443K]{\text{Conc. } H_2SO_4,} \underset{\text{Propene}}{CH_3CH=CH_2}$$

It may be noted that secondary alcohols dehydrate under mild conditions while tertiary alcohols are very easily dehydrated under very mild conditions. Thus, the overall **relative ease of dehydration of alcohols** is

$$3^\circ \text{ alcohol} > 2^\circ \text{ alcohol} > 1^\circ \text{ alcohol}.$$

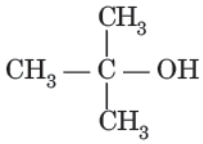
$$\underset{\substack{\text{Isopropyl alcohol}\\(2^\circ\text{alcohol})}}{CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3} \xrightarrow[438\text{ K} - 443\text{ K}]{H_2SO_4} \underset{\text{Propene}}{CH_3CH=CH_2}$$



Cyclohexanol (2°alcohol)

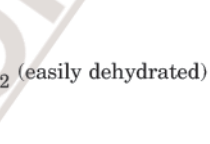
$$\xrightarrow[373–383\text{ K}]{H_3PO_4}$$

Cyclohexene



tert-Butyl alcohol (3°alcohol)

$$\xrightarrow[360\text{ K}]{H_2SO_4}$$



(easily dehydrated)

2-Methylpropene

Alkenes can also be prepared by heating alcohols with catalyst such as anhydrous zinc chloride ($ZnCl_2$) or alumina (Al_2O_3).

$$\underset{\text{Ethene}}{CH_3CH_2OH \xrightarrow[623\text{ K}]{\text{anhyd } Al_2O_3} CH_2=CH_2} + H_2O$$

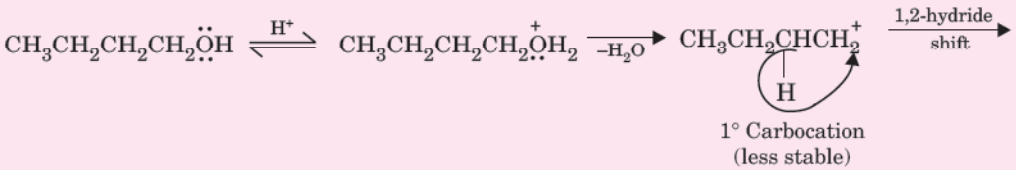
LEARNING PLUS

Rearrangement of Carbocations during dehydration of alcohols

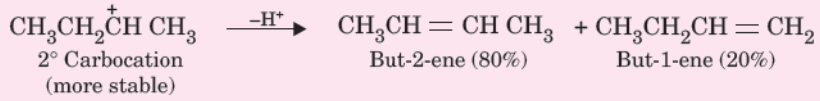
During dehydration of alcohols, sometimes unexpected alkenes are formed. This is because of the intermediate carbocations which have the property of rearrangement from a less stable to a more stable carbocation. This occurs either by **1,2-hydride** or **1,2-methyl shift**. This means that the carbocation initially formed can rearrange to form a more stable carbocation if the structure of the alkyl group permits. The carbocation formed, then loses a proton to form unexpected or the rearranged alkene. For example, the dehydration of butan-1-ol or butan-2-ol with conc. H_2SO_4 gives a mixture of but-1-ene and but-2-ene in which but-2-ene predominates. This can be explained by the rearrangement of the initially formed less stable 1° carbocation to the more stable 2° carbocation by 1, 2-hybride shift, which then loses a proton to form but-2-ene (major) and but-1-ene (minor) products.

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{H^+} \underset{\substack{\text{But-2-ene}\\\text{(major)}}}{CH_3CH=CHCH_3} + \underset{\substack{\text{But-1-ene}\\\text{(minor)}}}{CH_3CH_2CH=CH_2}$$

The formation of but-2-ene is because of rearrangement of carbocation, initially formed as:



1° Carbocation (less stable)



2° Carbocation (more stable)

But-2-ene (80%) + But-1-ene (20%)

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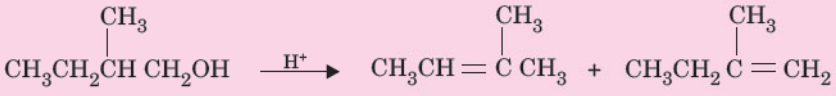
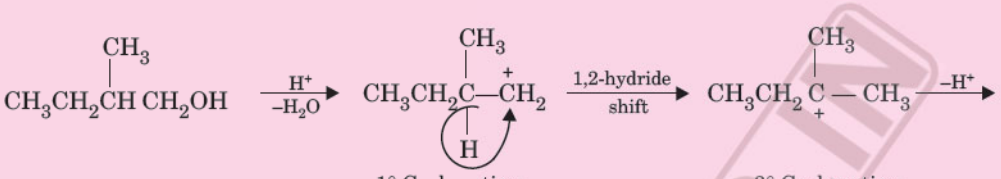
Similarly,

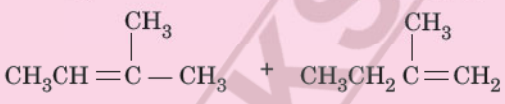


2-Methylbutan-1-ol — 2-Methylbut-2-ene (major) — 2-Methylbut-1-ene

This can be explained as:

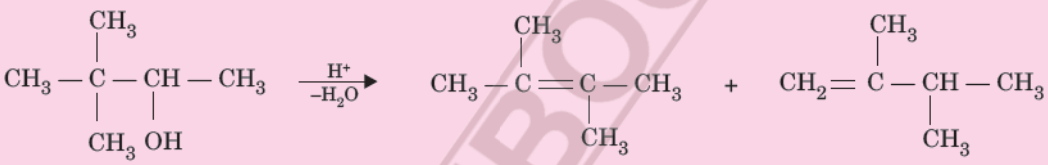


1° Carbocation (less stable) — 3° Carbocation (more stable)



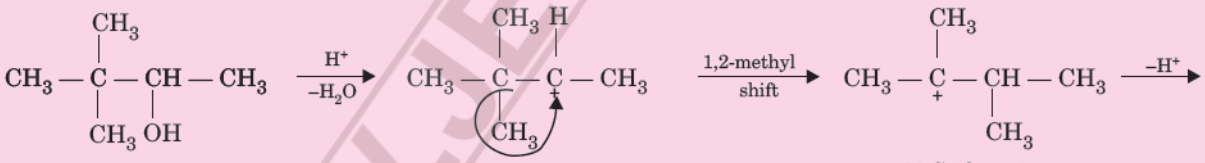
2-Methylbut-2-ene (major) — 2-Methylbut-1-ene

Similarly,

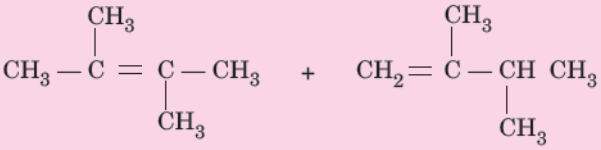


3, 3-Dimethylbutan-2-ol — 2, 3-Dimethylbut-2-ene (major) — 2, 3-Dimethylbut-1-ene

This can be explained as:



2° Carbocation (less stable) — 3° Carbocation (more stable)



2, 3-Dimethylbut-2-ene (major) — 2, 3-Dimethylbut-1-ene (minor)

It may be noted that when more than one alkene can be formed, the preferred product is the more stable one. It also follows **Saytzeff rule.**

Laboratory Preparation of Alkenes

In the laboratory, ethene is prepared by the acidic dehydration of ethyl alcohol. In this method, a mixture of ethyl alcohol and concentrated sulphuric acid in the ratio of 1 : 2 by volume is taken in a dropping funnel attached to a round bottomed flask. A small amount of aluminium sulphate and sand is also added in the round bottomed flask (Fig. 18).

Aluminium sulphate catalyses the reaction and sand prevents the frothing of the reaction mixture. The flask is heated on a sand bath when the reaction takes place and ethylene gas is produced. The gas produced is collected over water by the downward displacement of water.

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Purification of ethene. The gas obtained contains some impurities of sulphur dioxide (obtained by the reduction of sulphuric acid) and carbon dioxide (obtained by the oxidation of ethyl alcohol). Therefore, it is purified by passing the gas through a wash bottle containing concentrated solution of KOH which absorbs these gases.

$$SO_2 + 2KOH \longrightarrow K_2SO_3 + H_2O$$
$$CO_2 + 2KOH \longrightarrow K_2CO_3 + H_2O$$

The pure gas is then collected over water.

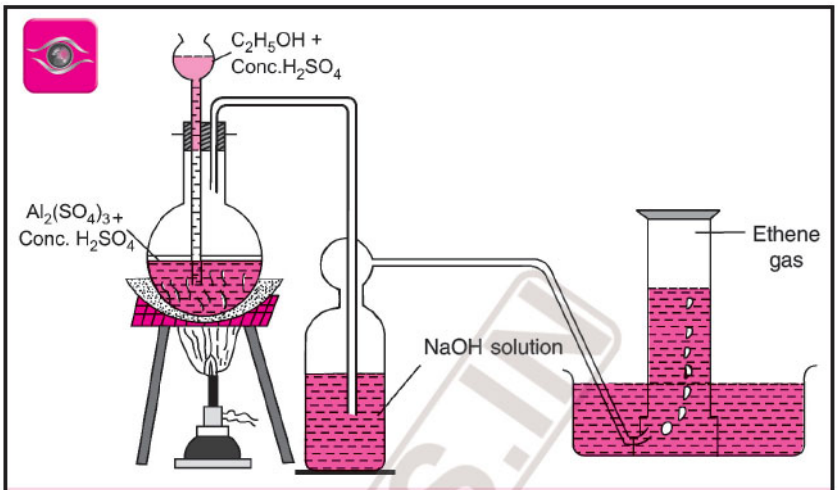


Fig. 18. Preparation of ethene in the laboratory.

5. By electrolysis of potassium salts of dicarboxylic acids. The electrolysis of potassium salts of dicarboxylic acids gives alkenes. This is called **Kolbe's reaction.**

$$\underset{\text{Potassium succinate}}{\begin{matrix}CH_2COOK\\|\\CH_2COOK\end{matrix}} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethylene}}{\begin{matrix}CH_2\\\|\\CH_2\end{matrix}} + 2CO_2 + H_2 + 2KOH$$

The reaction is believed to occur by the following steps :

$$\begin{matrix}CH_2COOK\\|\\CH_2COOK\end{matrix} \xrightarrow{\text{Ionization}} \begin{matrix}CH_2COO^-\\|\\CH_2COO^-\end{matrix} + 2K^+$$

$$2H_2O \rightleftharpoons 2OH^- + 2H^+$$

At anode

$$\begin{matrix}CH_2COO^-\\|\\CH_2COO^-\end{matrix} \xrightarrow{-2e^-} \left[\begin{matrix}CH_2COO\\|\\CH_2COO\end{matrix}\right] \longrightarrow \underset{\text{Ethene}}{\begin{matrix}CH_2\\\|\\CH_2\end{matrix}} + 2CO_2$$

At cathode

$$2H^+ + 2e^- \longrightarrow [2H] \longrightarrow H_2$$

Since the electrode potential of H^+ ions is higher than that of K^+ ions, therefore, H^+ ions are preferentially reduced to H_2 while K^+ ions remain in the solution.

Properties of Alkenes

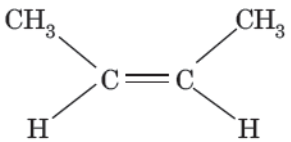
The important physical and chemical characteristics of the alkenes are discussed below :

Physical Properties

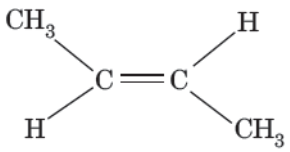
1. Physical state and smell. The first three alkenes (ethene, propene and butene) are gases at ordinary temperature. The alkenes containing 5 to 18 carbon atoms are liquids while the higher members of the family are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless.

2. Melting points. In general, alkenes have higher melting points than the corresponding alkanes. This is due to the reason that π-electrons of a double bond are more polarizable than σ-electrons of single bonds. As a result, the intermolecular forces of attraction are stronger in alkenes than in alkanes. Thus, the melting points of alkenes are higher than the corresponding alkanes. The melting and boiling points of alkenes, in general, increase with the increase in the molecular mass. However, these do not show regular gradation. Amongst isomeric alkenes, *trans-alkenes have higher melting points than their corresponding cis-isomers.*

For example,



cis-But-2-ene
(m.p. = 134.2 K)



trans-But-2-ene
(m.p. = 167.4 K)

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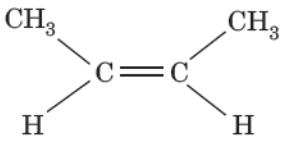
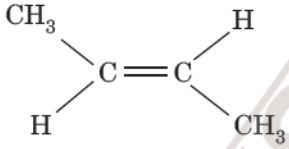
This is due to the reason that the molecules of *trans*-alkene are symmetrical and therefore, they can pack more closely in the crystal lattice than the molecules of *cis*-alkene. Therefore, larger amount of energy is required to break the crystal lattice of *trans*-alkene than the corresponding lattice of *cis*-alkene. Hence, *trans*-alkenes have higher melting points than the corresponding *cis*-isomers.

3. Boiling points. The boiling points of alkenes show a regular gradation with the increase in number of carbon atoms like alkanes. In general, for each added $-CH_2$ group the boiling point rises by 20–30°. The branched chain alkenes, however, have lower boiling points than the corresponding straight chain alkenes. Amongst the geometrical isomeric alkenes, *cis*-alkenes have higher boiling points than the corresponding *trans*-isomers.

For example,



cis-But-2-ene
(b.p. = 277 K)



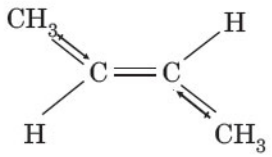
trans-But-2-ene
(b.p. = 274 K)

This is due to the reason that *cis*-alkene is more polar than *trans*-alkene. Therefore, trans-alkene has stronger dipole-dipole interactions and its boiling point is high.

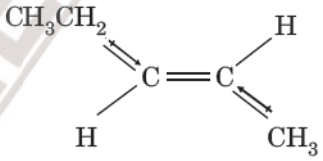
4. Dipole moments. Alkenes are weakly polar. The π-electrons of the double bond can be easily polarized. Therefore, their dipole moments are higher than those of alkanes.

The dipole moment of alkenes depends upon the position of the groups bonded to the two double bonded carbon atoms. The symmetrical trans alkenes are non polar and hence have zero dipole moment. In these alkenes, the dipole moments of individual bonds are equal and in opposite direction. Therefore, these get cancelled resulting zero dipole moment for the molecule.

However, unsymmetrical *trans*-alkenes have small dipole moment because the two dipoles oppose each other but they do not cancel out each other exactly since they are unequal.

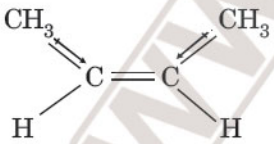


trans-But-2-ene
μ= 0

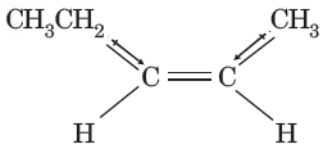


trans-Pent-2-ene
μ > 0
(small dipole moment)

On the other hand, both symmetrical and unsymmetrical *cis*-alkenes are polar and hence have finite dipole moments. This is because the two dipoles of individual bonds are on the same side and hence have a resultant dipole moment.

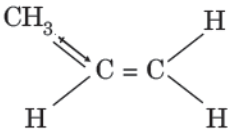


cis- But-2-ene
(μ= 0.25 D)

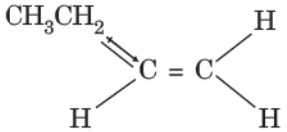


cis-Pent-2-ene
(μ > 0)

Similarly, unsymmetrical terminal alkenes such as propene and but-1-ene have some dipole moments because the polarity due to the alkyl group is not cancelled by the corresponding polarity in the opposite direction. For example,



Propene
(μ= 0.35D)



But-1-ene
(μ = 0.37D)

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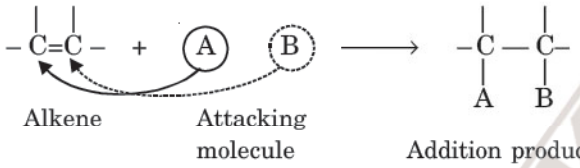
5. Solubility. Alkenes are lighter than water. These are insoluble in water because they are non-polar. However, they readily dissolve in organic solvents like alcohol, benzene, ether, carbon tetrachloride, etc.

Chemical Properties

Alkenes are characterized by the presence of double bond in their molecules. They are quite reactive chemically. This is due to the presence of π-bond. The π-electrons form an electron cloud which lies above and below the plane of σ-bonded carbon atoms. These π-electrons are therefore, more exposed and less tightly held between the two carbon atoms. Therefore, alkenes are attacked by reagents or compounds which are in search of electrons. These reagents are called **electrophilic reagents.** *Because of rich source of weakly held π-electrons, they show addition reactions in which the electrophiles add on to the C = C double bond to form addition products. The π-bond easily breaks during the chemical reactions of alkenes and results in the formation of two strong σ bonds. Hence alkenes have a tendency to undergo addition reactions which are of electrophilic nature.*



Apart from addition reactions alkenes also participate in the *oxidation*, *polymerization* and some *replacement reactions* of the alkyl group.

1. Addition Reactions

In these reactions, the attacking reagent is an *electrophile* i.e. either positively charged or electron deficient species. The negative centre for the electrophilic attack is made available by the high electron density of the double bond of alkene.

Mechanism :

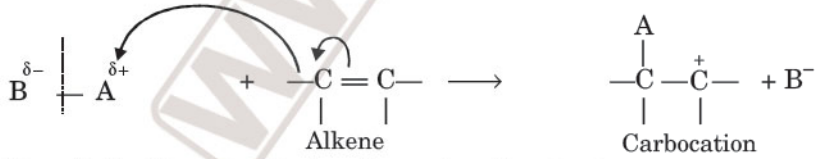
Electrophilic addition to alkenes

The electrophilic addition to alkenes takes place in the following two steps :

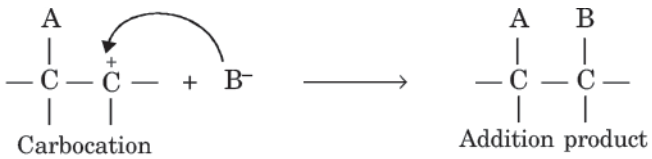
Step 1. In the first step, the attacking molecule (A – B) gets partially polarized. As this molecule approaches the π bond of the double bond, it begins to repel electron cloud of the attacking molecule away from it. As a result, the nearer end of the molecule acquires partial positive charge and farther end acquires partial negative charge ($\overset{\delta+}{A} - \overset{\delta-}{B}$).

At the same time, the double bond also undergoes electromeric effect resulting in the shift of the π electron pair to one of the carbon atoms making it negatively charged while the other carbon atom becomes positively charged. The positively charged atom (A^+) of the attacking molecule attacks the negative carbon of alkenes and forms a new C – A bond.

This leaves the other carbon atom with a +ve charge. The intermediate formed is called **carbocation.**



Step 2. In the second step, the anion B^- attacks the +ve carbon atom of the carbocation to form the addition product.



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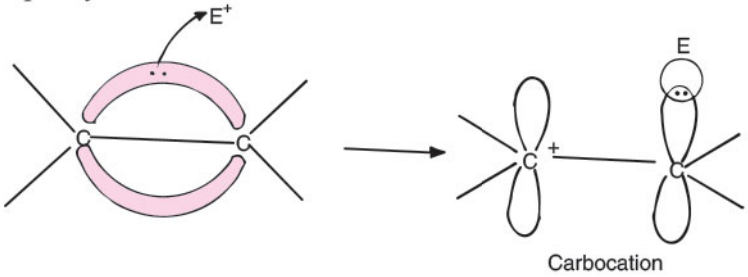
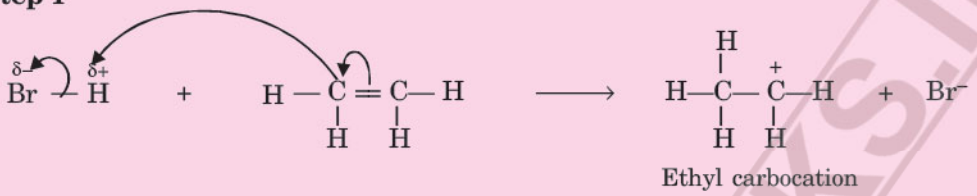
The first step may be shown as :



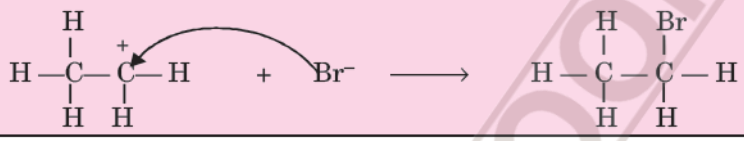
E^+ is an electrophile (say A)

For example, a specific example of addition of HBr to ethene may be shown below :

Step 1



Step 2



The important addition reactions of alkenes are :

***(a)* Addition of halogens.** Halogens (particularly chlorine and bromine) react with alkenes in the presence of an inert solvent (*e.g.* CCl_4) to form dihalogen derivatives :

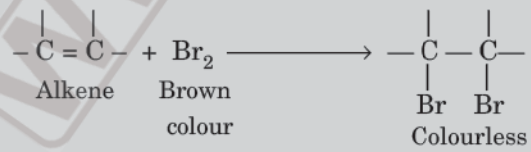
$$\underset{\text{Ethene}}{CH_2 = CH_2} + Br_2 \xrightarrow{CCl_4} \underset{\text{1, 2-Dibromoethane}}{CH_2(Br)-CH_2(Br)}$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + Br_2 \xrightarrow{CCl_4} \underset{\text{1, 2-Dibromopropane}}{CH_3-CH(Br)-CH_2(Br)}$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + Cl_2 \xrightarrow{CCl_4} \underset{\text{1, 2-Dichloropropane (Propylene chloride)}}{CH_3-CH(Cl)-CH_2(Cl)}$$

The reaction with fluorine is **explosive** whereas iodine does not react under normal conditions.

This reaction can be used as a **test for alkenes** because the brown colour of bromine will get decolourised by alkenes.



Note. It may be noted that the above test is also given by alkynes (triple bonded compounds). In fact, this test is used to detect the presence of double bond or triple bond in a compound (*i.e.*, unsaturation).

Mechanism : Addition of Br_2 to alkenes

The addition of Br_2 to an alkene (*e.g.*, ethene) occurs in the following steps :

(*i*) **Polarisation of bromine molecule.** Bromine molecule is a non-polar molecule because the electron pair between two bromine atoms is equally shared between two atoms. As the bromine molecule approaches the ethene molecule, the π-electron cloud of the carbon-carbon double bond repels the electron cloud of the bromine molecule. Consequently, the electrons of the bromine molecule get displaced away from the bromine atom

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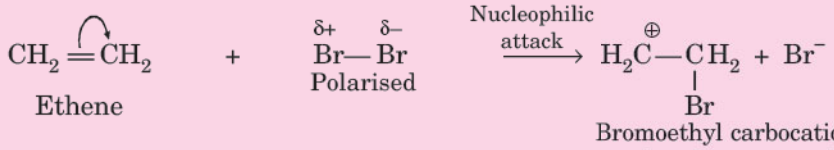
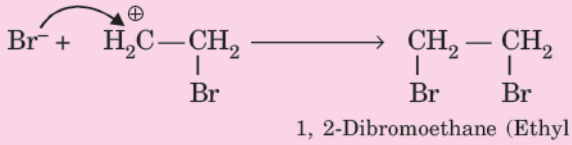
nearer to the ethene molecule. Therefore, the bromine atom nearer to double bond becomes positively polarised while the other atom gets negatively polarised. The positively polarised bromine atom attacks the π-electron cloud of the double bond giving rise to a carbocation and a negative bromide ion.

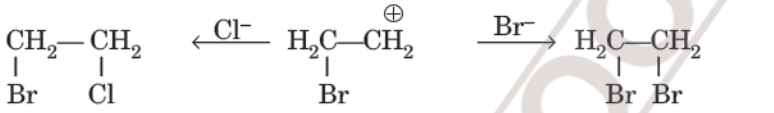


(*ii*) **Attack of bromide ion.** The Br^- ion then attacks the positively charged carbon atom to form the addition product.



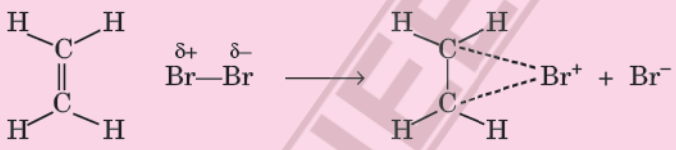
Evidence in favour of Ionic Mechanism

The mechanism of addition reaction is ionic in nature. This can be supported by adding some Cl^- ion to the reaction mixture. The product obtained is a mixture of 1, 2–dibromoethane and 1–bromo–2–chloroethane. The formation of 1–bromo–2–chloroethane occurs due to attack of Cl^- ion on the carbocation and also establishes the ionic nature of the mechanism. The formation of chloro derivative along with 1, 2-dibromoethane from the intermediate carbocation is shown below :

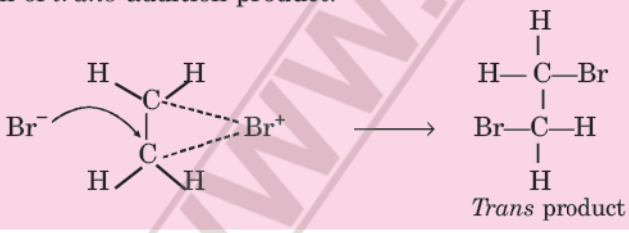


Trans bromination

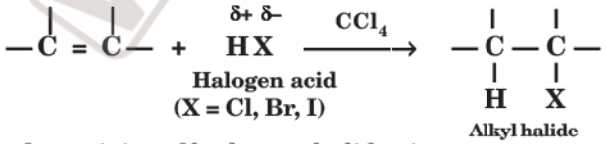
It is interesting to note that addition of bromine leads to *trans addition* product. The *trans* addition product can be explained with the help of a **cyclic intermediate** called bromonium ion in the initial step. In the first step polarised bromine atom attacks the ethene molecule forming cyclic bromonium ion as :



The attack of the Br^- ion on this cyclic ion can take place from the opposite side only resulting in the formation of *trans* addition product.



(*b*) Addition of halogen acids (hydrohalogenation). Alkenes react with halogen acids (HCl, HBr or HI) to form alkyl halides.



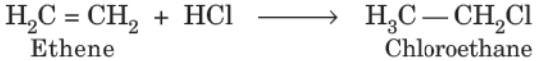
The order of reactivity of hydrogen halides is :

$$HI > HBr > HCl$$

The actual product formed depends upon whether the alkene is symmetrical or unsymmetrical as discussed below.

(i) Addition reactions of HX to symmetrical alkenes.

In these reactions, only one product is theoretically possible. For example,



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$$\underset{\text{But-2-ene}}{H_3CHC = CHCH_3} + HBr \longrightarrow \underset{\text{2-Bromobutane}}{H_3CCH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3}$$

(*ii*) Addition reactions of HX to unsymmetrical alkenes

When the alkene is *unsymmetrical*, then two products are possible. For example, when propene is treated with HBr, both 1-bromopropane and 2-bromopropane may be formed as the products.

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + HBr \longrightarrow \begin{cases} \longrightarrow CH_3-CH_2-CH_2Br & \text{1-Bromopropane} \\ \longrightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3 & \text{2-Bromopropane} \end{cases}$$

In these cases, the addition is governed by **Markovnikov rule** proposed by a Russian chemist Markovnikov. It states that

during the addition across unsymmetrical multiple bond, the negative part of the addendum (attacking molecule) joins with the carbon atom which carries lesser number of hydrogen atoms while the positive part goes to the carbon atom with larger number of hydrogen atoms.

For example, in case of propene, 2-bromopropane is major product.

$$\underset{\text{Propene}}{CH_3CH = CH_2} + HBr \longrightarrow \underset{\text{2-Bromopropane (90\%)}}{CH_3-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3} + \underset{\text{1-Bromopropane (10\%)}}{CH_3-\underset{\displaystyle H}{\underset{|}{C}}H-\underset{\displaystyle Br}{\underset{|}{C}}H_2}$$

However, a small percentage of the isomer in which halogen atom (negative part) is attached to carbon with more number of hydrogen atoms is also formed.

Exception to Markovnikov rule

Kharasch and Mayo (1933) observed that when HBr is added to an unsymmetrical double bond in the presence of organic peroxides (R — O — O — R *e.g.* benzoyl peroxide, $C_6H_5CO\,OO\,CO\,C_6H_5$), the reaction takes place opposite to the Markovnikov rule. This is known as **anti-Markovnikov rule** or **peroxide effect.** It is also called **Kharasch effect**. According to anti Markovnikov rule, during the addition of HBr to an unsymmetrical alkene the Br atom will join to the carbon carrying more hydrogen atoms while H atom will go to the other carbon atom. For example,

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + HBr \xrightarrow{(R-O-O-R)} \underset{\text{1-Bromopropane}}{CH_3-\underset{\displaystyle H}{\underset{|}{C}}H-\underset{\displaystyle Br}{\underset{|}{C}}H_2}$$

It may be noted that only **HBr shows peroxide effect.** HF, HCl and HI do not exhibit peroxide effect and therefore, addition of HF, HCl and HI takes place according to Markovnikov's rule even in the presence of peroxides.

Thus, to **sum up**, the addition of HBr to propene gives 2-bromopropane in the absence of peroxides and 1-bromopropane in the presence of peroxides as :

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + HBr \longrightarrow \begin{cases} \xrightarrow[\text{Peroxides}]{\text{No}} \underset{\text{2-Bromopropane}}{CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3} & \textbf{Markovnikov rule} \\ \xrightarrow{\text{Peroxides}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2\,Br} & \textbf{Anti-Markovnikov rule} \end{cases}$$

Thus, according to Markovnikov rule, the main products in the reactions can easily be **predicted**. For example, addition of hydrogen halides to higher alkenes give the main products as :

$$\underset{\text{2-Methylpropene}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2} + HCl \longrightarrow \underset{\text{2-Chloro-2-methylpropane}}{CH_3-\underset{\displaystyle Cl}{\underset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3}$$

$$\underset{\text{2-Methylbut-2-ene}}{CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3} + HBr \longrightarrow \underset{\text{2-Bromo-2-methylbutane}}{CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3}$$

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Mechanism : Explanation of Markovnikov rule

In order to understand Markovnikov rule, let us consider the attack of electrophile (H^+) on the propene molecule. The two intermediate carbocations which are possible are :

$CH_3–CH = CH_2$ + H^+ (Attacking electrophile)

Propene

- $CH_3 - \overset{+}{C}H - CH_3$ — 2° Carbocation (I) (more stable) — Joins with terminal C atom
- $CH_3 - CH_2 - CH_2^+$ — 1° Carbocation (II) (less stable) — Joins with central C atom

The carbocation that is formed with a large proportion is decided on the basis of its **relative stability.** Now, we know that 2° carbocation is more stable than 1° carbocation, therefore, the attack of (H^+) ion on propene results in the formation of more stable carbocation (I). This ion further reacts with Br^- to form the addition product :

$$CH_3\,\overset{+}{C}H\,CH_3 + Br^- \longrightarrow CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$$

Carbocation (I)

This product is in accordance with Markovnikov rule. Thus, Markovnikov rule may also be stated in the alternative form as :

The electrophilic addition to an unsymmetrical alkene always occurs through the formation of a more stable carbocation intermediate.

Thus, the complete mechanism for the addition of HBr to propene may be explained as :

$$HBr \xrightarrow{\text{Ionization}} H^+ + Br^-$$

$$\underset{\text{Propene}}{CH_3—CH = CH_2} + H^+ \longrightarrow \underset{\text{2° Carbocation}}{CH_3—\overset{+}{C}H—CH_3}$$

$$CH_3\overset{+}{C}HCH_3 + Br^- \longrightarrow CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$$

2-Bromopropane

Note : 2° carbocation will be formed instead of 1° carbocation because it is more stable.

Peroxide effect

Kharasch and Mayo discovered that the addition of HBr to unsymmetrical alkene in the presence of organic peroxides (such as benzoyl peroxide, $C_6H_5\ CO–O–O–COC_6H_5$) takes place opposite to the Markovnikov rule. This is known as **anti-Markovnikov rule** or **peroxide effect**. According to this rule, the Br atom will join to that carbon atom which carries more hydrogen atoms, while the H atom will go to other carbon atom.

Thus,

$$CH_3—CH = CH_2 + HBr \xrightarrow{\text{Peroxides}} \underset{\text{1-Bromopropane (90\%)}}{CH_3—CH_2—CH_2Br} + \underset{\text{2-Bromopropane (10\%)}}{CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3}$$

Explanation for anti–Markovnikov rule.

The addition of HBr to alkenes in the presence of peroxides occurs by **free radical mechanism.** In this mechanism, the first two steps result into generation of free radical $Br^\bullet$. Then, it adds to double bond in such a way to give more stable free radical. Then this free radical abstracts a $H^\bullet$ free radical from HBr to complete the addition. The various steps of the mechanism are :

(1) $C_6H_5—\overset{\displaystyle O}{\overset{\|}{C}}—O—O—\overset{\displaystyle O}{\overset{\|}{C}}—C_6H_5 \xrightarrow{\text{Homolysis}} 2C_6H_5—\overset{\displaystyle O}{\overset{\|}{C}}—\dot{O} \longrightarrow 2C_6\dot{H}_5 + 2CO_2$

Benzoyl peroxide — Free radical

(2) $C_6\dot{H}_5 + H—Br \xrightarrow{\text{Homolysis}} C_6H_6 + \dot{Br}$

Free radical

(3) $\dot{Br} + CH_3—CH=CH_2$

- $CH_3—\dot{C}H—CH_2Br$ — 2° Free radical (I) (more stable)
- $CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—\dot{C}H_2$ — 1° Free radical (II) (less stable)

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Because the 2° free radical is more stable than 1° free radical, it will be preferably formed.

(4) $CH_3-\dot{C}H-CH_2Br + H-Br \longrightarrow CH_3-CH_2-CH_2Br + Br^{\cdot}$

Preferred free radical — 1-Bromopropane (Major product)

Then steps (3) and (4) are repeated again and again to form the desired product.

Exceptional behaviour of HBr. It is interesting to note that peroxide effect is applicable only to HBr and not to HF, HCl or HI. This can be understood on the basis of energy changes in the propagation step using different halogen atoms :

Step 3 : $\dot{X} + CH_3-CH=CH_2 \longrightarrow CH_3-\dot{C}H-CH_2X$

X = F	ΔH = – 209 kJ/mol
X = Cl	ΔH = – 101 kJ/mol
X = Br	ΔH = – 42 kJ/mol
X = I	ΔH = + 12 kJ/mol

Step 4 : $H-X + CH_3-\dot{C}H-CH_2X \longrightarrow CH_3-CH_2-CH_2X + \dot{X}$

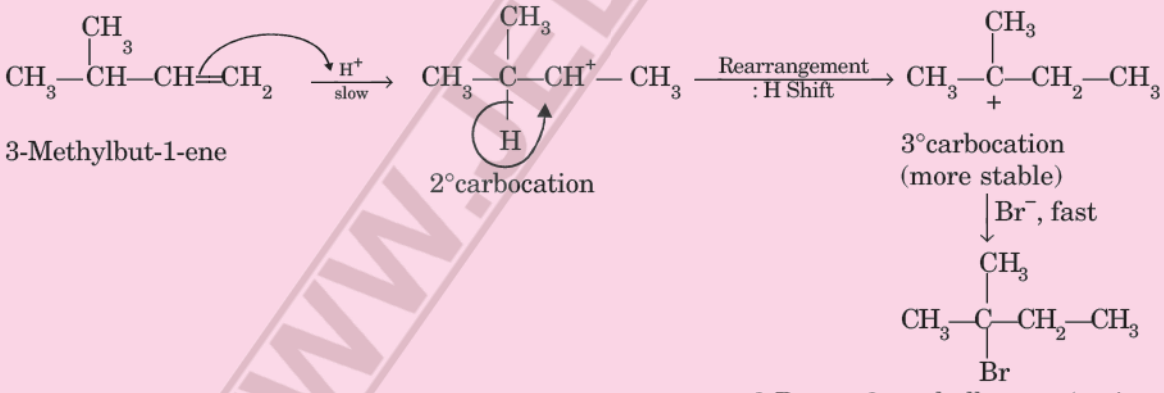
X = F	ΔH = + 159 kJ/mol
X = Cl	ΔH = + 27 kJ/mol
X = Br	ΔH = – 37 kJ/mol
X = I	ΔH = – 106 kJ/mol

From the above data, it is clear that only with HBr both the steps are **exothermic** and hence, free radical mechanism is possible. With HF or HCl, the attack of these do not follow free radical mechanism because the second step involving the attack of carbon radical with HF or HCl is **endothermic** and not favourable. In other words, homolysis of HF or HCl does not take place. In case of HI, the homolysis of HI is possible as evident from step 4 but the attack of I to propene does not take place (Step 3 is endothermic). So, the free radical I will combine with similar free radical to form I_2 molecule. Thus, **peroxide effect is observed only in case of HBr.**

LEARNING PLUS

Rearrangement of Carbocations

We have learnt that addition of HBr to alkenes occurs through the formation of carbocation. Sometimes it is observed that the product formed is different from the one expected. This is because of the **rearrangement of carbocation.** The carbocation initially formed can rearrange to form a more stable carbocation if the structure of the alkyl group permits. For example,



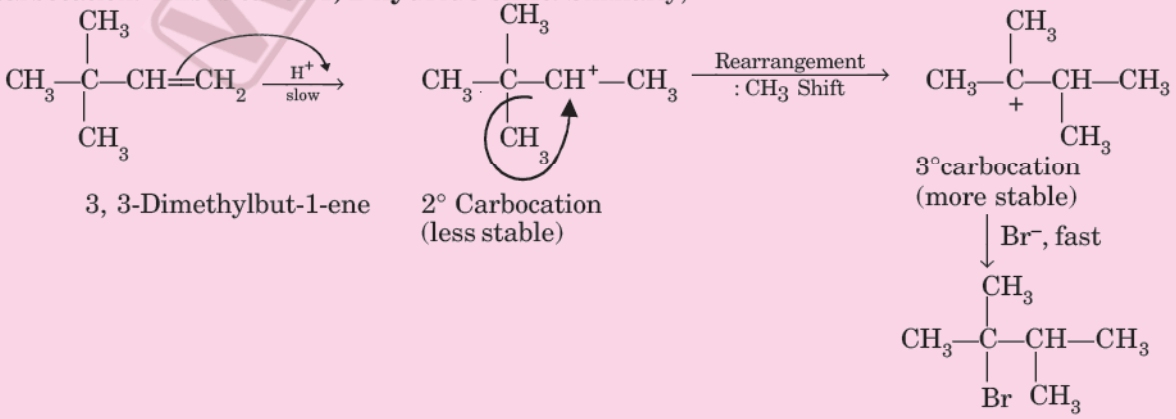
3-Methylbut-1-ene

2°carbocation

3°carbocation (more stable)

2-Bromo-2-methylbutane (major product)

We observe that 2° carbocation rearranges to 3° carbocation because 3° carbocation is more stable than 2° carbocation. This is called **1, 2-hydride shift**. Similarly,



3, 3-Dimethylbut-1-ene

2° Carbocation (less stable)

3°carbocation (more stable)

2-Bromo-2, 3-dimethylbutane

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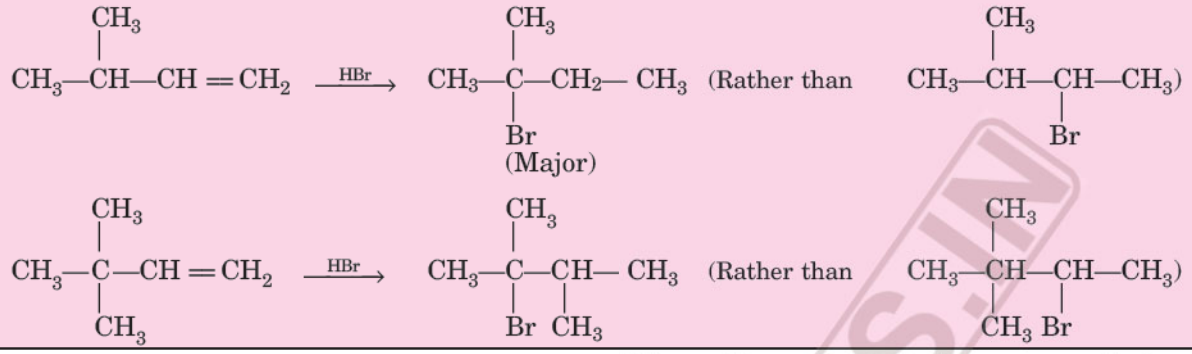
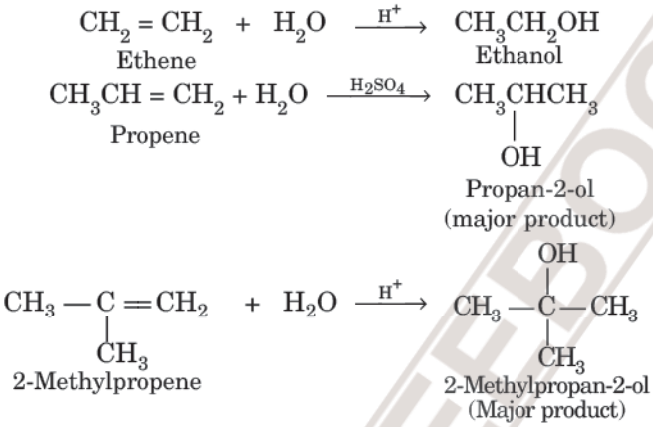
This is called **1, 2-methyl shift**. So, if the structure permits, the rearrangement occurs in such a way that a less stable carbocation is converted into a more stable carbocation. This rearrangement can occur only if a 1, 2-shift of hydrogen or alkyl can form a stable carbocation.The products obtained are those formed from the rearranged carbocations (major product) and not from the original ones. Thus,

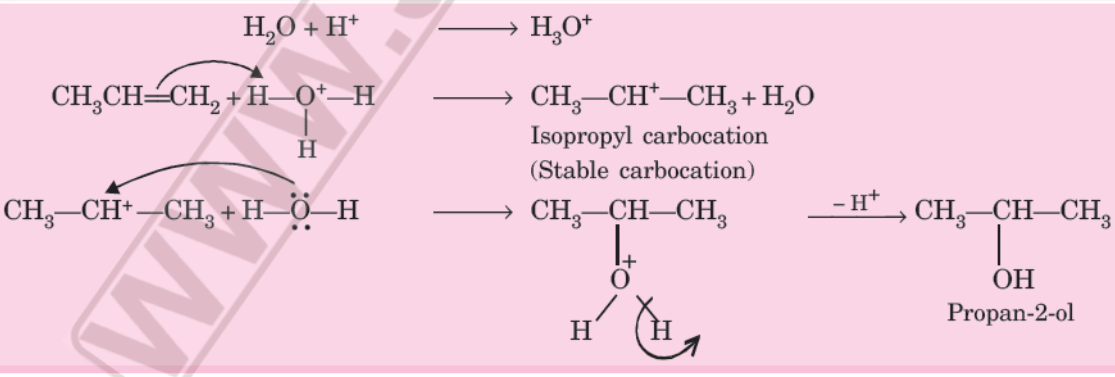

CH3—CH(CH3)—CH=CH2 HBr CH3—C(CH3)(Br)—CH2—CH3 (Major) (Rather than CH3—CH(CH3)—CH(Br)—CH3)
CH3—C(CH3)2—CH=CH2 HBr CH3—C(CH3)(Br)—CH(CH3)2 (Rather than CH3—CH(CH3)—CH(CH3)—CH2Br)

(c) Addition of water (hydration of alkenes). Water adds to alkenes in the presence of mineral acids. In this case also, the addition occurs in accordance with Markovnikov's rule. For example,

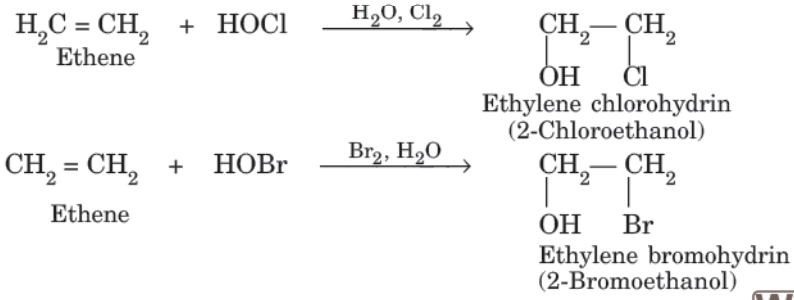


This reaction is also known as **hydration reaction.**

Mechanism : Addition of water to alkenes



(d) Addition of hypohalous acid. Alkenes react with hypohalous acids (HOCl or HOBr) or halogen Cl_2 or Br_2 in the presence of H_2O to give halohydrins. In this reaction, the addition occurs according to Markovnikov rule (halogen is positive part and —OH is negative part).



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$$CH_3-CH=CH_2 + HOCl \xrightarrow{Cl_2,\ H_2O} CH_3-\underset{OH}{CH}-\underset{Cl}{CH_2}$$

Propene

Propylene chlorohydrin
(1-Chloropropan-2-ol)

In the case of propene, the reaction occurs according to Markovnikov rule.
The order of reactivity of different hypohalous acids (HOX) or X_2 | H_2O is
Cl_2 | H_2O (HOCl) > Br_2 | H_2O (HOBr) > I_2 | H_2O (HOI)

Mechanism : Addition of Cl_2 | H_2O to alkenes

$$CH_3-CH=CH_2 + \overset{\delta+}{Cl}-\overset{\delta-}{Cl} \xrightarrow{Slow} CH_3-CH^+-CH_2Cl$$

$$CH_3-CH^+-CH_2Cl + H_2\ddot{O}: \xrightarrow{Fast} CH_3-\underset{\overset{|}{O^+}}{\overset{H}{\diagdown}\ \diagup\ H}-CH_2Cl \xrightarrow{-H^+} CH_3-\underset{OH}{CH}-CH_2Cl$$

1-Chloropropan-2-ol

(e) Addition of sulphuric acid. Cold and concentrated sulphuric acid adds to alkenes forming alkyl hydrogen sulphate.

$$H_2C=CH_2 + HOSO_2OH \longrightarrow H_3C-CH_2OSO_2OH \text{ or } CH_3CH_2.HSO_4$$

Ethene — Ethyl hydrogen sulphate

$$CH_3-CH=CH_2 + HOSO_2OH \longrightarrow CH_3-\underset{OSO_2OH}{CH}-CH_3$$

Propene — Isopropyl hydrogen sulphate

Mechanism : Addition of H_2SO_4 to alkenes

The mechanism of the reaction may be written as :

$$H_2SO_4 \longrightarrow H^+ + \bar{O}SO_2OH$$

$$CH_3CH=CH_2 + H^+ \longrightarrow CH_3-CH^+-CH_3$$

Isopropylcarbocation
(Stable carbocation)

$$CH_3-CH^+-CH_3 + O^-SO_2OH \longrightarrow CH_3-\underset{OSO_2OH}{CH}-CH_3$$

In case of unsymmetrical alkenes, the addition also occurs according to Markovnikov rule and $-SO_2OH$ group adds to the carbon linked to lesser number of hydrogen atoms.

Alkyl hydrogen sulphates on boiling with water undergo hydrolysis to form alcohols.

$$CH_3CH_2OSO_2OH + H_2O \xrightarrow{Boil} CH_3-CH_2OH + H_2SO_4$$

Ethanol

$$CH_3\underset{OSO_2OH}{CH}-CH_3 + H_2O \xrightarrow{Boil} CH_3-\underset{OH}{CH}-CH_3 + H_2SO_4$$

Isopropyl alcohol

Thus, alkenes can be converted to corresponding alcohols on treatment with sulphuric acid and subsequent hydrolysis.

$$CH_2=CH_2 \xrightarrow{H_2SO_4\ (cold)} CH_3CH_2OSO_2OH \xrightarrow[Boil]{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

2. Oxidation Reactions

Alkenes give different products on oxidation under different conditions.

(a) Combustion. Alkenes burn in oxygen or air to give carbon dioxide, water and a large amount of heat is evolved.

$$\underset{\text{Ethene}}{C_2H_4} + 3O_2 \longrightarrow 2CO_2 + 2H_2O\ ; \quad \Delta H = -1411.0\ kJ\ mol^{-1}$$

$$\underset{\text{Alkene}}{C_nH_{2n}} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O\ ; \quad \Delta H = -\text{ve}$$

They form explosive mixture with air or oxygen and burn with luminous flame.

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(*b*) Oxidation with potassium permanganate. Alkenes react with **cold, dilute** aqueous, neutral or alkaline potassium permanganate solution to form 1, 2-diols called **glycols.** The glycols contain two –OH groups on adjacent carbon atoms. This reaction of addition of two hydroxyl groups to each end of double bond is called **hydroxylation** of the double bond.

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

$$\underset{\text{Ethene}}{CH_2=CH_2} + \underbrace{H_2O + O}_{\text{from } KMnO_4} \xrightarrow[273\ K]{\text{Alk. } KMnO_4} \underset{\text{Ethane-1, 2-diol (Ethylene glycol)}}{CH_2(OH)-CH_2(OH)}$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O + O \xrightarrow[\text{(cold)}]{\text{Alk. } KMnO_4} \underset{\substack{\text{Propane-1, 2-diol}\\ \text{(Propylene glycol)}}}{CH_3-CH(OH)-CH_2(OH)}$$

$$\underset{\text{But-2-ene}}{CH_3CH=CHCH_3} + H_2O + O \xrightarrow[\text{Cold}]{\text{Alk. } KMnO_4} \underset{\text{Butane-2, 3-diol}}{CH_3-CH(OH)-CH(OH)-CH_3}$$

The alkaline potassium permanganate solution is known as **Baeyer's reagent**. It has bright pink colour. It oxidises alkenes to glycols which is colourless. Therefore, the pink colour of Baeyer' s reagent is discharged and brown precipitate of manganese dioxide is formed. This reaction is used as a test for the presence of double bond in a molecule. This is also known as **Baeyer's test.**

$$\underset{\text{Alkene}}{-C=C-} + \underset{\text{Pink colour}}{KMnO_4} \xrightarrow{H_2O} \underset{\text{Colourless}}{-C(OH)-C(OH)-} + \underset{\text{Brown ppt}}{MnO_2}$$

(*c*) Oxidation with hot potassium permanganate solution. When alkene is treated with hot acidic potassium permanganate or potassium dichromate solution the alkene gets split up at the double bond forming carboxylic acids or ketones. This is also called **oxidative cleavage of alkenes.** For example,

$$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{\text{Hot } KMnO_4} \underset{\substack{\text{Methanoic acid}\\ \text{(Formic acid)}}}{H-C(=O)-OH} \xrightarrow[\text{Heat}]{[O]} 2CO_2 + 2H_2O$$

With terminal alkenes (double bond present at the end of carbon chains), one of the products is always methanoic acid (formic acid) which on further oxidation gives carbon dioxide and water.

$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{Hot } KMnO_4]{[O]} \underset{\substack{\text{Ethanoic acid}\\ \text{(Acetic acid)}}}{CH_3-C(=O)-OH} + CO_2 + H_2O$$

$$\underset{\text{2-Methylpropene}}{CH_3-C(CH_3)=CH_2} \xrightarrow[\text{Hot } KMnO_4]{[O]} \underset{\substack{\text{(Acetone)}\\ \text{Propanone}}}{CH_3-C(=O)-CH_3} + CO_2$$

With **non terminal alkenes,** carboxylic acids or ketones or both of these are obtained depending upon the nature of alkene. For example.

$$\underset{\text{But-2-ene}}{CH_3CH=CHCH_3} \xrightarrow[\text{Hot } KMnO_4]{[O]} \underset{\text{2 molecules of ethanoic acid}}{CH_3COOH + CH_3COOH}$$

$$\underset{\text{Pent-2-ene}}{CH_3CH_2CH=CHCH_3} \xrightarrow[\text{Hot } KMnO_4]{[O]} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

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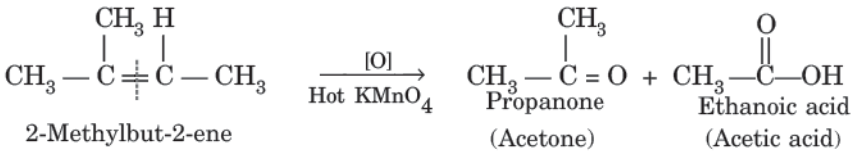
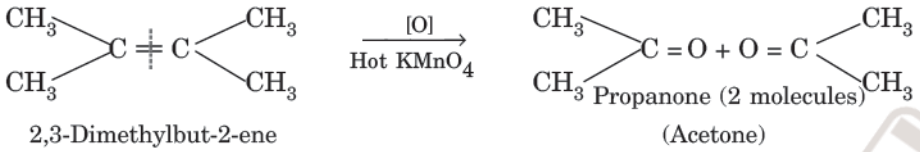
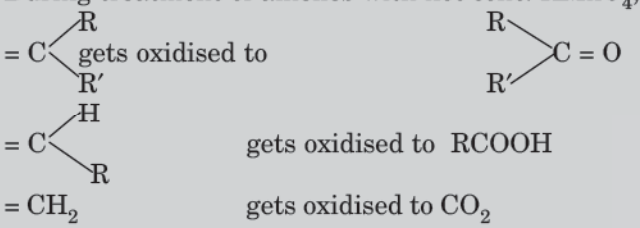




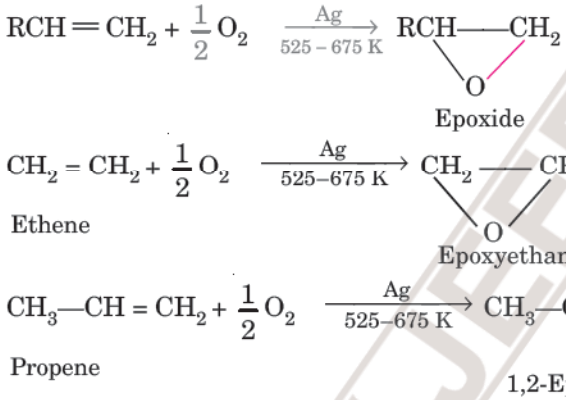
The reaction also occurs in the presence of sodium periodate ($NaIO_4$)

As a memory aid :

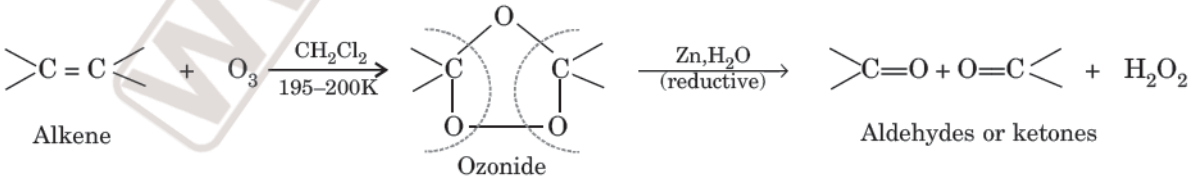
During treatment of alkenes with hot conc. $KMnO_4$, the products formed are :



(*d*) Catalytic oxidation. Alkenes react with oxygen in the presence of silver catalyst at 525 K to 675 K to form epoxyalkanes or epoxides. (alkene oxides)

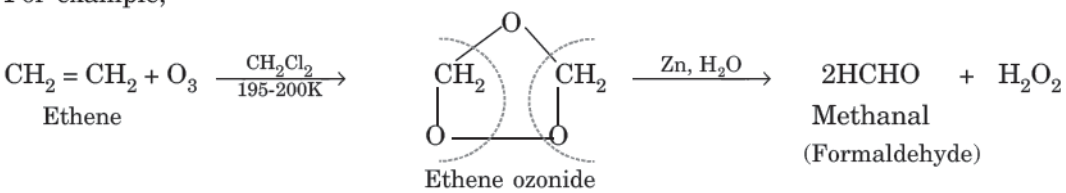


(*e*) Oxidation with ozone. Alkenes are oxidised with ozone to form *ozonides* which are unstable compounds. These are reduced with zinc and water forming aldehydes and ketones. The reaction is called **ozonolysis.** For example, when ozone is passed through a solution of an alkene in some inert solvent such as dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$) or carbon tetrachloride (CCl_4) at a low temperature (195 – 200 K) it oxidises alkene to ozonide. Ozonides are unstable and explosive compounds. Therefore, they are not generally isolated but are reduced *in situ* with zinc dust and water to give aldehydes and ketones depending upon the structure of the alkene.



It is clear that if the carbon forming the double bond carries a hydrogen atom attached to it, it gives rise to **aldehydes** otherwise **ketones** are formed.

For example,



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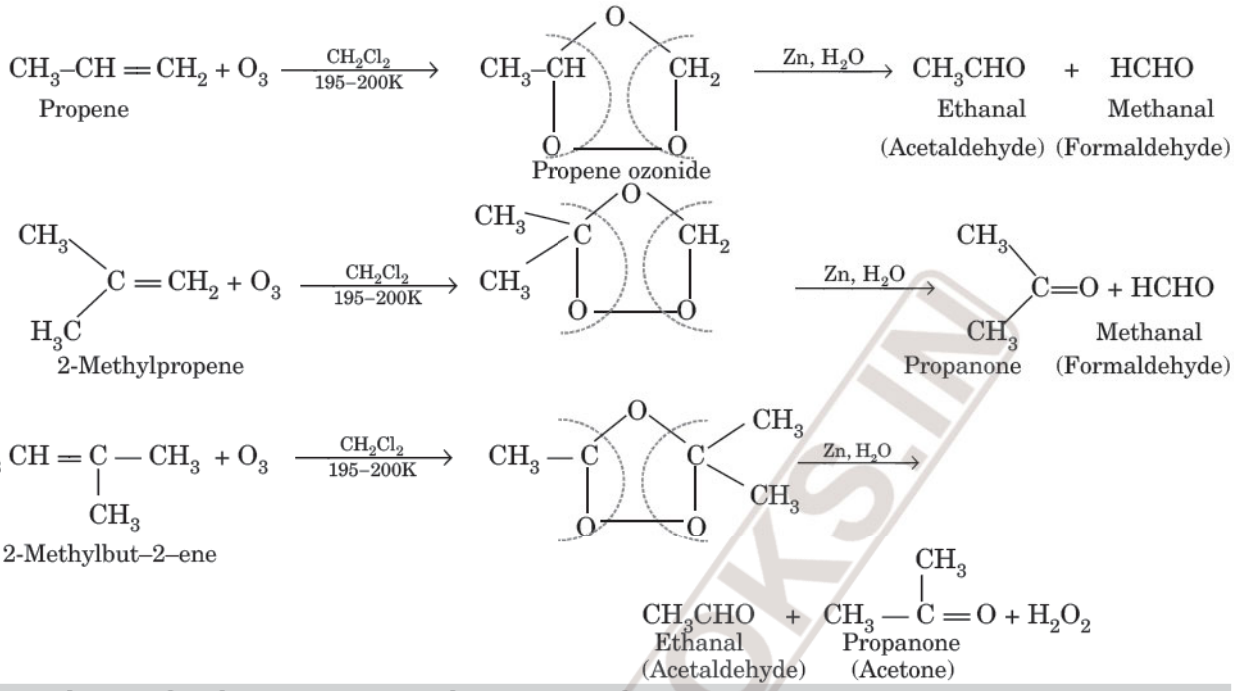
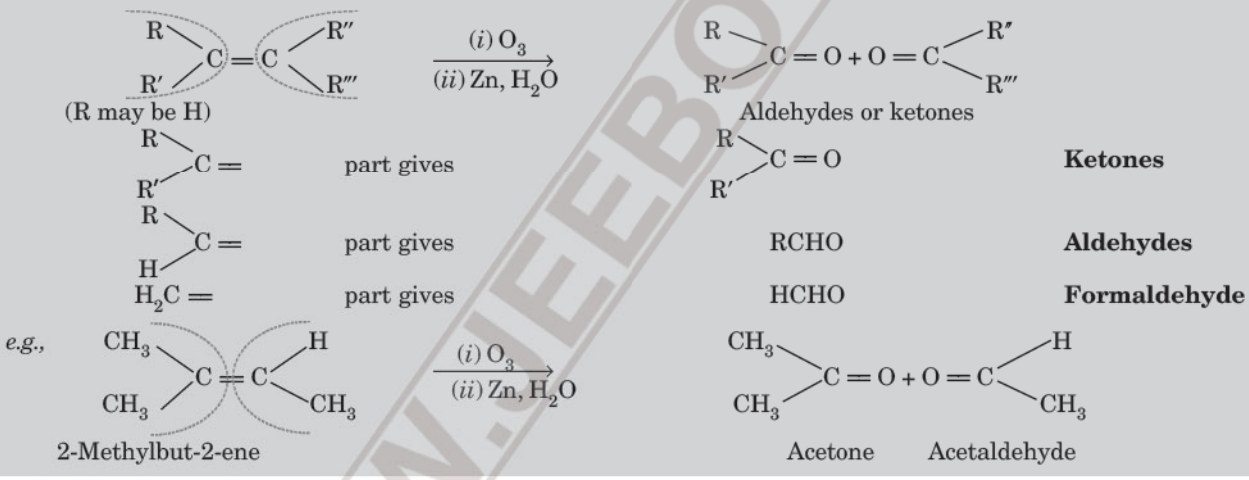


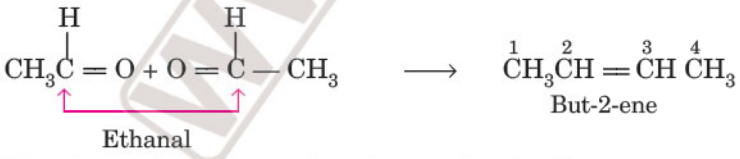
In a simple way, the above reaction may be represented as :



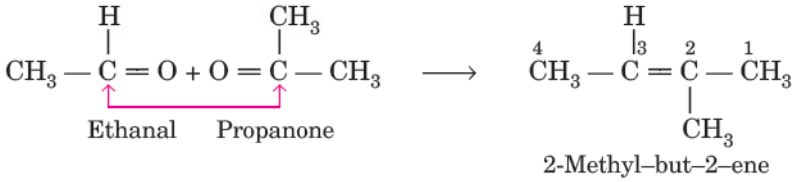
Applications of ozonolysis.

The process of ozonolysis is quite useful to locate the position of double bond in an alkene molecule. *The double bond is obtained by joining the carbon atoms of the two carbonyl compounds*. For example,

(*i*) Let the product of ozonolysis be two molecules of *ethanal* (acetaldehyde).



(*ii*) Let the product of ozonolysis be a molecule of *ethanal* (acetaldehyde) and *propanone* (acetone).



Thus, it may be *noted*

Bromine water test and Baeyer's test are used for detecting the presence of double bond while ozonolysis helps in locating the position of double bond.

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LEARNING PLUS

Hydroboration oxidation. This is another method of hydration of alkenes where hydration takes place anti to Markovnikov rule. Alkenes react with diborane (B_2H_6) to form trialkyl boranes which on oxidation with alkaline H_2O_2 give alcohols. This reaction involves two reactions; addition of borane (BH_3) to double bond called *hydroboration* followed by *oxidation* and *hydrolysis* to give alcohol.

For example,

$$\underset{\text{Propene}}{H_3C{-}CH=CH_2} + \underset{\text{Diborane}}{(BH_3)_2} \longrightarrow \underset{n\text{-Propyl borane}}{H_3C{-}CH_2CH_2BH_2} \xrightarrow{CH_3CH=CH_2} \underset{\text{Di-}n\text{-propylborane}}{(CH_3{-}CH_2CH_2)_2BH}$$

$$\underset{\text{Di-}n\text{-propylborane}}{(CH_3{-}CH_2CH_2)_2BH} \xrightarrow{CH_3CH=CH_2} \underset{\text{Tri-}n\text{-propylborane}}{(CH_3{-}CH_2CH_2)_3B} \xrightarrow{H_2O_2,\ OH^-} \underset{\text{Boric acid}}{B(OH)_3} + \underset{\text{Propan-1-ol}}{3CH_3{-}CH_2CH_2OH}$$

The net addition of the reaction is the addition of a water molecule to a double bond opposite to that of Markovnikov rule. This may be represented as :

$$\underset{\text{Propene}}{H_3C{-}CH=CH_2} \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6} \underset{\text{Propan-1-ol}}{H_3C{-}CH_2{-}CH_2OH}$$

$$\underset{\text{Pent-1-one}}{CH_3(CH_2)_2CH=CH_2} \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6} \underset{\text{Pentan-1-ol}}{CH_3(CH_2)_2CH_2CH_2OH}$$

The hydroboration reaction was discovered by Herbert C. Brown, who was awarded Noble Prize in 1980 for the synthetic uses of the reaction.

3. Reduction. Alkenes react readily with hydrogen in the presence of a catalyst to give alkanes. This reaction is called **catalytic hydrogenation.** Alkenes add hydrogen in presence of Raney nickel (activated form of nickel), palladium or platinum catalyst at room temperature or ordinary nickel at 523–573 K (Sabatier Sendern's reduction).

$$\underset{\text{Ethene}}{H_2C=CH_2} + H_2 \xrightarrow{\text{Pt, Pd or Ni}} \underset{\text{Ethane}}{H_3C{-}CH_3}$$

$$\underset{\text{Propene}}{CH_3{-}CH=CH_2} + H_2 \xrightarrow{\text{Pt, Pd or Ni}} \underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3}$$

This reaction is used in the manufacture of vanaspati ghee from vegetable oils.

4. Polymerisation Reactions

Polymerisation is a ***process in which a large number of simple (same or different) molecules combine to form a bigger molecule of higher molecular mass. The small molecules*** are called **monomers** ***while the bigger molecules*** are called **macromolecules** or **polymers.**

Alkenes undergo polymerisation to give very important compounds. For example,

***(i)* Polymerisation of ethene.** When ethene is heated in the presence of traces of oxygen at 473 - 673 K under high pressure (1500 atm) a large number of molecules combine to form **polyethylene** or **polyethene**.

$$\underset{\text{Ethene}}{n\ CH_2=CH_2} \xrightarrow[\text{traces of oxygen}]{473-673\ \text{K/Pressure}} \underset{\text{Polyethene}}{\left(-CH_2-CH_2-\right)_n}$$

Here n may have very large value varying from 600 – 1000 K. Polyethene is *extremely useful in industry.* It is mainly employed to make toys, bottles, electric goods, plastic bags, refrigerator dishes, T.V. cabnets, etc.

***(ii)* Polymerisation of propene.** Propene on heating at high temperature and high pressure in the presence of benzoyl peroxide as initiator or by Ziegler-Natta catalyst, polymerises to polypropene.

$$\underset{\text{Propene}}{n\ CH_3{-}CH=CH_2} \xrightarrow[\text{Catalyst}]{\text{High temp/pressure}} \underset{\text{Polypropene}}{\left[-CH_2-\overset{\overset{CH_3}{|}}{CH}-\right]_n}$$

Polyprene is harder and stronger polymer than polythene. It is used for making milk crates, plastic buckets, automobile mouldings, seat covers, carpet fibres, ropes, heat shrinkable wraps for records and other articles.

***(iii)* Polymerisation of vinyl chloride.** Vinyl chloride polymerises to give polyvinyl chloride commonly known as P.V.C.

$$\underset{\text{Vinyl chloride}}{n\ CH_2=\overset{\overset{Cl}{|}}{CH}} \xrightarrow{\text{Polymerisation}} \underset{\text{Polyvinyl chloride (PVC)}}{\left[-CH_2-\overset{\overset{Cl}{|}}{CH}-\right]_n}$$

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It is commonly used for making P.V.C. pipes which are used in the underground electric fittings, in making raincoats and also in special type of curtains, etc.

(*iv*) Polymerisation of styrene. Styrene ($C_6H_5 — CH = CH_2$) polymerises to give polystyrene.

Styrene Polystyrene

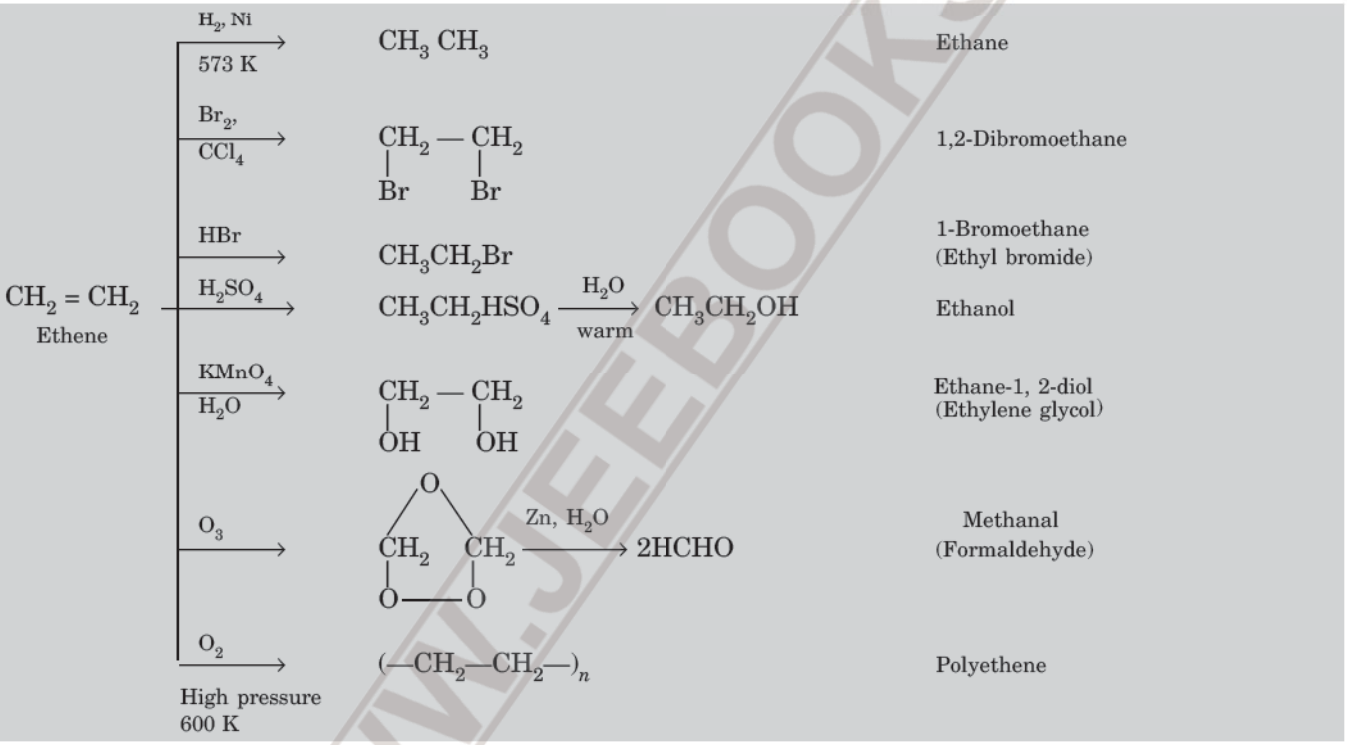
Polystyrene is used for making packing materials and also for the toys.

(*v*) Polymerisation of tetrafluoroethylene. Tetrafluoroethylene polymerises to teflon.

$$\underset{\text{Tetrafluoroethylene}}{nF_2C = CF_2} \xrightarrow{\text{Polymerisation}} \underset{\text{Polytetrafluoroethylene (Teflon)}}{[—F_2C—CF_2—]_n}$$

Teflon is thermally stable and is very *little reactive chemically.* It is, therefore, used for coating the inner surfaces of the non-sticking cooking pans.

The important reactions of **ethene** are summarized below :

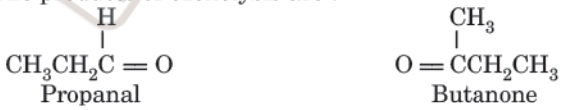


SOLVED EXAMPLES

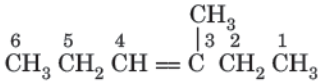
Example 17.

The reductive ozonolysis of an alkene gave butanone and propanal. Write the structure of alkene and its IUPAC name. ***N.C.E.R.T.***

Solution: The products of ozonolysis are :



The alkene will be (remove oxygen atoms and make double bond between the carbonyl carbon atoms).



IUPAC name : 3-Methylhex-3-ene

Example 18.

Write the products and their IUPAC names obtained when hex-1-ene reacts with HBr
(i) in the absence of peroxide (ii) in the presence of peroxide

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Solution:

$$CH_2{=}CHCH_2CH_2CH_2CH_3 + HBr \xrightarrow[\text{Markovnikov addition}]{\text{No peroxide}} CH_3{-}\underset{\underset{Br}{|}}{CH}CH_2CH_2CH_2CH_3$$

Hex-1-ene — 2-Bromohexane

$$CH_2{=}CHCH_2CH_2CH_2CH_3 + HBr \xrightarrow[\text{Anti Markovnikov addition}]{\text{Peroxide}} CH_2\underset{\underset{Br}{|}}{CH}CH_2CH_2CH_2CH_3$$

Hex-1-ene — 1-Bromohexane

❑ **Example 19.**

Ozonolysis of an alkene 'X' followed by decomposition with water and a reducing agent gave a mixture of two isomers of the formula C_3H_6O. Give the structure of the alkene and its IUPAC name.

Solution: The two isomers of the molecular formula C_3H_6O are :

$$CH_3CH_2\underset{\underset{H}{|}}{C}{=}O$$ Propanal

$$O{=}\underset{\underset{CH_3}{|}}{C}{-}CH_3$$ Propanone

The alkene is

$$CH_3CH_2CH{=}\underset{\underset{CH_3}{|}}{C}{-}CH_3$$

IUPAC name : 2-Methylpent-2-ene

❑ **Example 20.**

Propanal and pentan-3-one are the ozonolysis products of an alkene. What is the structural formula and IUPAC name of alkene. ***N.C.E.R.T.***

Solution: The products are :

$$CH_3CH_2CH{=}O$$ Propanal

$$O{=}\underset{\underset{CH_2CH_3}{|}}{C}CH_2CH_3$$ Pentan-3-one

Alkene is

$$CH_3CH_2\,CH{=}\underset{\underset{C_2H_5}{|}}{C}CH_2CH_3$$

3- Ethylhex-3-ene

Practice Problems

16. What is the formula of teflon ?

17. A compound (C_7H_{14}) on ozonolysis gives ethanal and pentan-3-one. What is the structure of alkene?

18. How will propene react with HBr (*i*) in the presence of peroxide (*ii*) in the absence of any peroxide ?

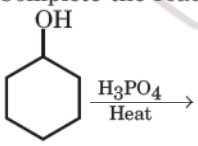
19. Name two tests to test the presence of double bond in a compound.

20. Name an alkene which on reductive ozonolysis produces only acetone.

21. Complete the reaction :

$$CH_2 = CH_2 \xrightarrow{\text{alk. } KMnO_4}$$

22. Complete the reaction:



Answers to Practice Problems

16. Polytetrafluoroethene

17. $CH_3CH = C(C_2H_5)\,CH_2CH_3$

18. (*i*) $CH_3CH_2CH_2Br$ (*ii*) $CH_3CH(Br)CH_3$

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19. (*i*) decolourises brown colour of bromine.
(*ii*) decolourises pink colour of Baeyer's reagent.

20. 2, 3-Dimethyl-but-2-ene

21. $CH_2(OH)\,CH_2(OH)$

22. $+ H_2O$

CHEMISTRY OF ALKYNES

Alkynes are unsaturated hydrocarbons having carbon-carbon triple bonds in their molecules. Their general formula is C_nH_{2n-2}.The simplest member of this class is ethyne (C_2H_2) which is popularly known on acetylene.

STRUCTURE OF TRIPLE BOND

Ethyne is the simplest molecule of alkyne series. In this case, each carbon atom is *sp* hybridised forming two *sp* hybrid orbitals. These two *sp* hybrid orbitals lie along straight line and the bond angle between them is 180°. The two unhybridised *p*-orbitals are perpendicular to each other and also to the axis of the hybridised orbitals.

In the triple bond formation, one *sp* hybridised orbital of one carbon atom overlaps axially (head on) with the similar *sp* hybrid orbital of the other carbon atom to form σ bond. Each of the two unhybridised orbitals of one carbon overlaps sidewise with the similar orbital of the other carbon atom to form two weak π bonds. The remaining *sp* hybrid orbital of each carbon atom overlaps with 1*s* orbital of hydrogen to form C –H bond. The structure of the triple bond is being illustrated by the orbital structure of ethyne shown in Fig. 19.

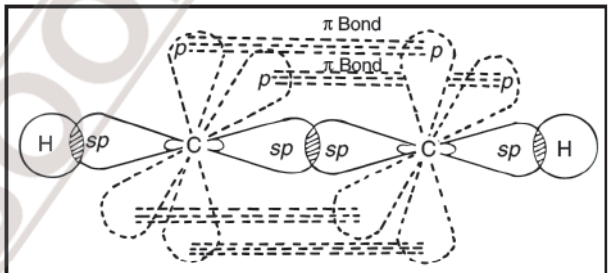


Fig. 19. Structure of acetylene.

Thus, carbon to carbon triple bond is made up of one σ bond and two π bonds. If one π electron cloud is visualised as lying above and below the internuclear axis representing σ bond, the other π electron cloud lies in front and in back of the line [Fig. 20 (*a*)]. The overall orbital picture of the molecule is, that of a cylindrical electron cloud symmetrically distributed around the internuclear axis [Fig 20 (*b*)].

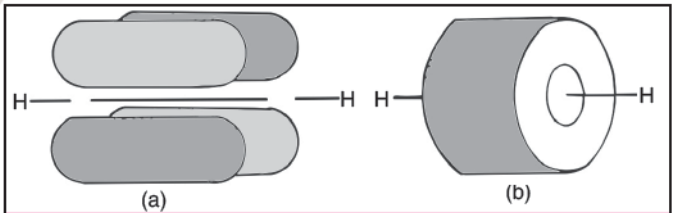
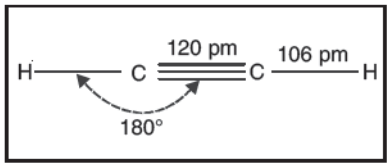


Fig. 20 Cylindrical π electron cloud

The electron diffraction studies have shown that the —C≡C— bond length is 120 pm and C–H bond length is 106 pm. While the H—C≡C— bond angle is 180°, the strength of the —C≡C— bond 823 kJ mol^{-1}.



Thus, the strength of the triple bond in alkyne is more than that of the double bond (681kJ mol^{-1}) in alkene and C—C single bond (348 kJ mol^{-1}) in alkanes. In fact , greater energy is released in the orbital overlap when triple bond is formed than in case of double bond.

It may be pointed out that carbon—carbon bond length in acetylene is 120pm in comparison to 134 pm in ethene and 154 pm in ethane molecule. This means that C≡C bond is shorter than that of C=C bond and C—C bond. It has been explained on the basis of extent of overlapping of orbitals. The C≡C bond involves the formation of one σ bond and two π bonds. For the formation of additional π bond in acetylene as compared to ethylene, the bonding orbitals of carbon atoms have to come close together which results in shortening of bond distance. Moreover, the effective size of *sp* hybrid orbitals is smaller than that of sp^2 hybrid orbitals. This also decreases the distance between the constituent carbon atoms.

The value of the bond angle and the orbital structure of alkynes clearly indicate that they are **linear molecules.** Hence, there is no restricted or hindered rotation about the triple bond. Alkynes, therefore, do not show any *geometrical isomerism*.

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NOMENCLATURE OF ALKYNES

In common systems, the alkynes are named as derivatives of acetylene (Unit 12). For example.

In IUPAC system, they are named as derivatives of corresponding alkanes replacing 'ane' by the suffix 'yne'. As already discussed the following rules should be followed :

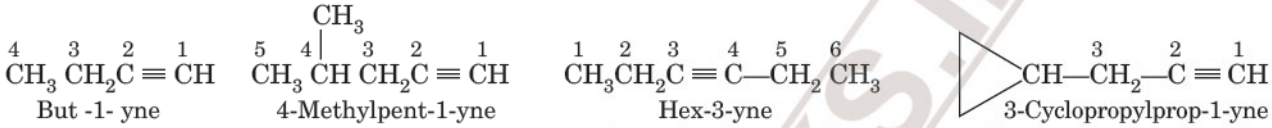
(*i*) *The longest continuous chain should include both the carbon atoms of the triple bond.*

(*ii*) *The* ***suffix*** *used for alkyne is* ***–yne.***

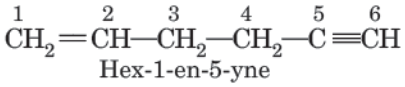
(*iii*) *The chain is numbered from the end which gives the lower* ***number*** *to the first carbon atom of the triple bond.*

(*iv*) *The position of the substituents are indicated.*

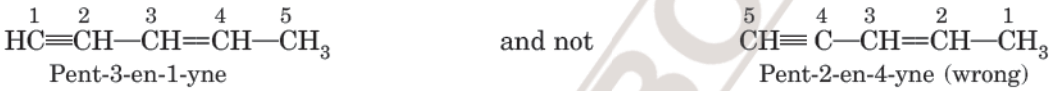
For example,



If both double bond and triple bond are present in the molecule such that both get the same number while numbering from either side then *double bond is given preference*.



However, if double bond and triple bound are present at non-equivalent positions, then *lowest set of locants rule is followed*. For example,



ISOMERISM IN ALKYNES

Alkynes exhibit the following structural isomerisms :

(*i*) Chain isomerism. *The isomers differ in the chain of carbon atoms.* For example, the molecule having molecular formula C_5H_8 shows chain isomers as :

(*ii*) Position isomerism. *Alkynes having more than four carbon atoms show position isomerism.* For example,

The structural isomers of C_5H_8 may be written as :

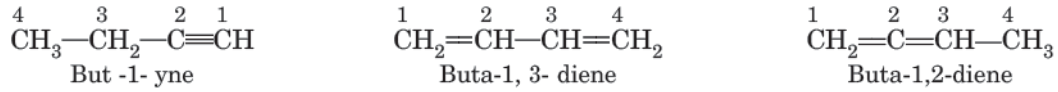
(*i*) $CH_3—CH_2—CH_2—C \equiv CH$ Pent-1-yne

(*ii*) $CH_3—CH(CH_3)—C \equiv CH$ 3-Methylbut-1-yne

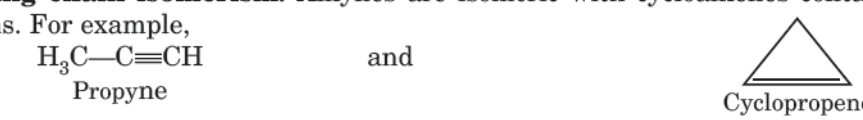
(*iii*) $CH_3—CH_2—C \equiv C—CH_3$ Pent-2-yne

Structures (*i*) and (*ii*) are chain isomers while structure, (*i*) and (*iii*) are position isomers.

(*iii*) Functional isomerism. Alkynes having four or more carbon atoms are functional isomers of dienes i.e., compounds containing two double bonds. For example,



(*iv*) Ring chain isomerism. Alkynes are isomeric with cycloalkenes containing the same number of carbon atoms. For example,



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$H_3C—CH_2—C\equiv CH$ (But-1-yne) or $CH_3—C\equiv C—CH_3$ (But-2-yne) and (Cyclobutene) are ring-chain isomers.

No geometrical isomerism. It may be noted that the alkynes are linear molecules and —C ≡ C—H bond angle is 180°. Therefore, alkynes do not show **geometrical isomerism.**

PREPARATION AND PROPERTIES OF ALKYNES

Preparation of Alkynes

The alkynes are prepared by the following general methods :

1. Action of water on calcium carbide. Ethyne (acetylene) is prepared in the laboratory as well as on industrial scale by the action of water on calcium carbide.

$$CaC_2 + 2H_2O \longrightarrow \underset{\text{Ethyne (Acetylene)}}{HC\equiv CH} + Ca(OH)_2$$

Calcium carbide required for this purpose is obtained by heating calcium oxide (from limestone) and coke in an electric furnace at 2275 K.

$$\underset{\text{Calcium carbonate}}{CaCO_3} \xrightarrow{\text{Heat}} \underset{\text{Calcium oxide}}{CaO} + CO_2$$

$$CaO + 3C \xrightarrow{2275\ K} \underset{\text{Calcium carbide}}{CaC_2} + CO$$

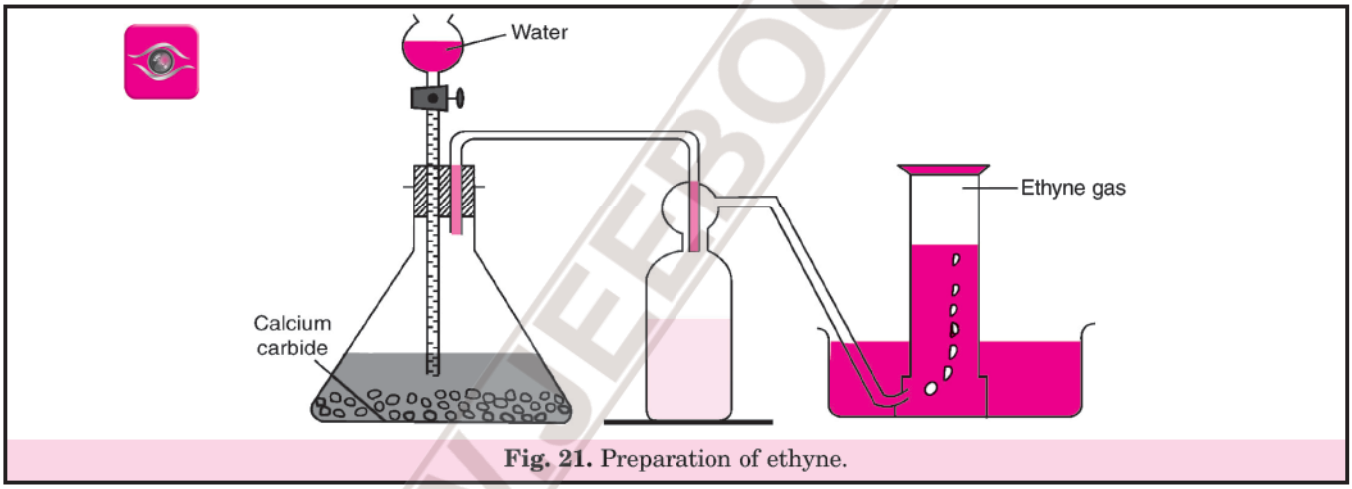

Fig. 21. Preparation of ethyne.

In the laboratory, ethyne is commonly prepared from calcium carbide. In this method, a few pieces of calcium carbide are taken in a conical flask fitted with a dropping funnel and a delivery tube. *The air present in the flask is replaced by oil gas because acetylene forms an explosive mixture with air.* Water is taken in the dropping funnel and allowed to fall into the flask dropwise. The reaction takes place vigorously and ethyne gas is produced which is collected over water.

Purification. The gas obtained by the above method generally contains the impurities of hydrogen sulphide and phosphine due to the contamination of calcium sulphide and calcium phosphide in calcium carbide. These impurities are removed by bubbling the gas through acidified copper sulphate solution.

$$H_2S + CuSO_4 \longrightarrow \underset{\text{(Black ppt.)}}{CuS} + H_2SO_4$$

$$2PH_3 + 3CuSO_4 \longrightarrow \underset{\substack{\text{Cupric phosphide}\\ \text{(Black ppt.)}}}{Cu_3P_2} + 3H_2SO_4$$

2. By dehydrohalogenation of dihalides or vicinal dihalides. Alkynes are prepared by double **dehydrohalogenation** of vicinal dihalides (containing two halogen atoms on the adjacent carbon atoms) with strong base like alcoholic solution of potassium hydroxide or sodamide in liquid ammonia.

$$\underset{\substack{\text{vic–dihalide}}}{\begin{matrix} R—CH—CH—R' \\ \quad | \quad\ | \\ \quad X \quad X \end{matrix}} \xrightarrow{\text{alc. KOH}} \underset{\text{Alkyne}}{RC\equiv CR'}$$

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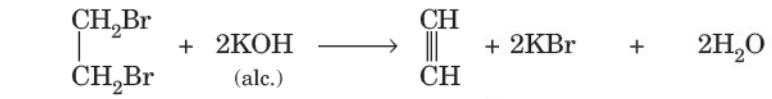
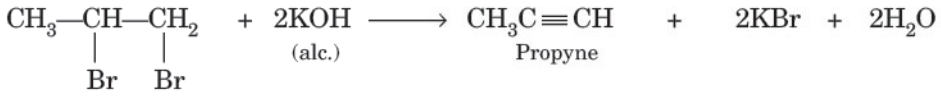
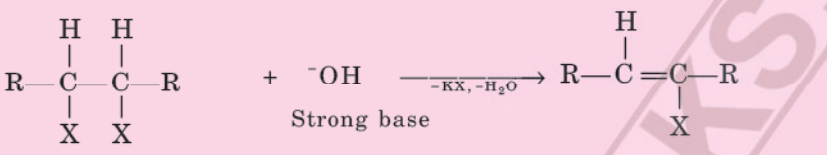


1,2-Dibromoethane (Ethylene dibromide)

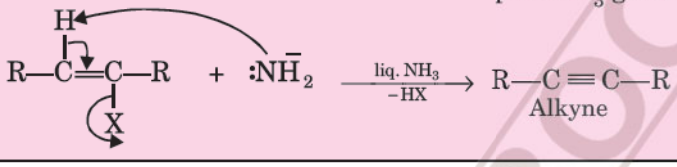


1,2-Dibromopropane (Propylene dibromide)

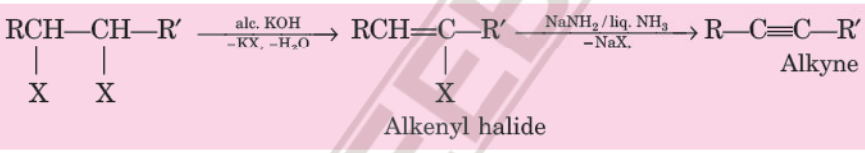
The reaction, in fact, occurs in two steps. The first step gives haloalkene and under suitable conditions this may be isolated. For example, vicinal dihalides on treatment with alcoholic potassium hydroxide give alkenyl halide.



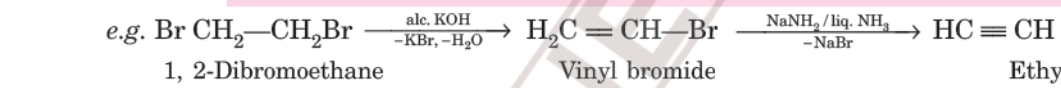
The haloalkene on treatment with sodamide in liquid NH_3 gives alkyne.



The reaction may be written as :



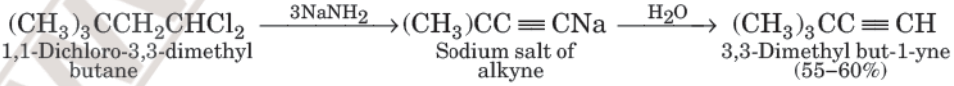
e.g.



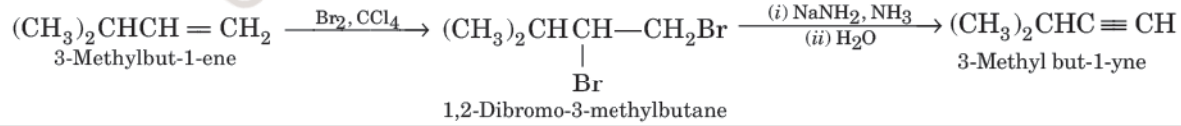
1, 2-Dibromoethane — Vinyl bromide — Ethyne

It may be noted that second step is more difficult and a stronger base like sodamide is needed for the second step which removes proton from alkenyl halides more easily. Depending upon the conditions, these two dehydrohalogenation reactions may be carried out as separate reactions or they may be carried out in a single mixture.

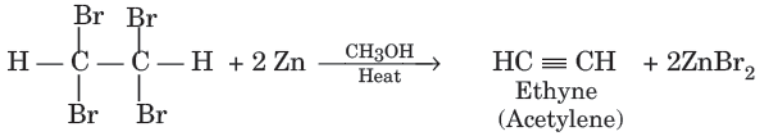
The strong base sodamide, is capable of effecting both dehydrohalogenations in a single reaction mixture. For this two molar equivalents of sodamide must be used. However, if the product is terminal alkyne, three molar equivalents of sodamide would be used. This is because terminal alkyne product will react with sodium amide and one equivalent of base in addition to the two equivalents required for double dehydrohalogenation is needed. Treatment of the sodium salt of alkyne with water or acid gives corresponding alkyne. For example.



Vicinal dihalides are prepared by addition of chlorine or bromine to alkenes and therefore, alkenes can serve as starting materials for the preparation of alkynes as shown below :



3. By the action of zinc on tetrahalogen derivatives of alkanes (tetrahalides). On treatment with zinc in methanol, tetrahalides get dehalogenated to give alkynes.



1,1,2,2-Tetrabromoethane

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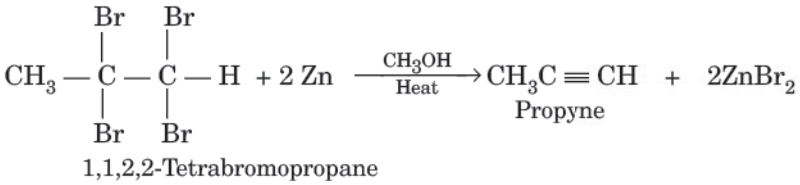
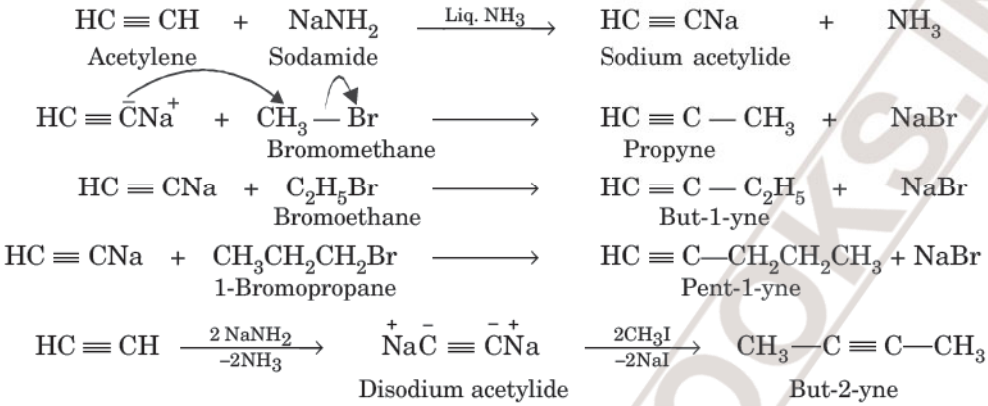


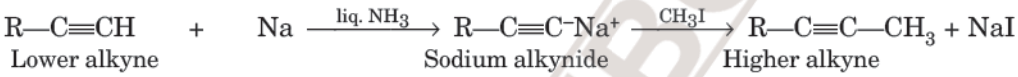
1,1,2,2-Tetrabromopropane

This method is mainly used for the purification of alkynes or protection of a triple bond because the tetrabromides are themselves obtained from alkynes.

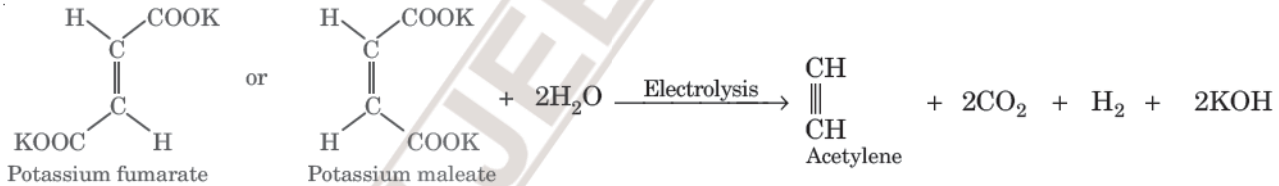
4. Higher alkynes from acetylene. Higher alkynes are prepared from acetylene by treating its sodium salt with alkyl halide. The sodium salt is prepared by treating acetylene with sodium metal at 475 K or by the action of sodamide ($NaNH_2$) on acetylene in liquid ammonia at 196 K.


HC ≡ CH + NaNH2 → HC ≡ CNa + NH3
Acetylene Sodamide Liq. NH3 Sodium acetylide
HC ≡ C⁻Na⁺ + CH3 — Br → HC ≡ C — CH3 + NaBr
Bromomethane Propyne
HC ≡ CNa + C2H5Br → HC ≡ C — C2H5 + NaBr
Bromoethane But-1-yne
HC ≡ CNa + CH3CH2CH2Br → HC ≡ C—CH2CH2CH3 + NaBr
1-Bromopropane Pent-1-yne
HC ≡ CH 2 NaNH2 −2NH3 Na⁺C⁻ ≡ C⁻Na⁺ 2CH3I −2NaI CH3—C ≡ C—CH3
Disodium acetylide But-2-yne

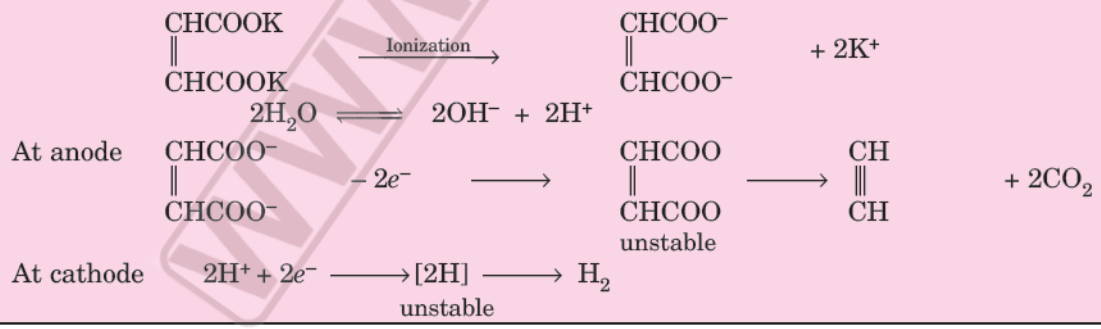
This method is mainly used to convert lower alkynes to higher alkynes.



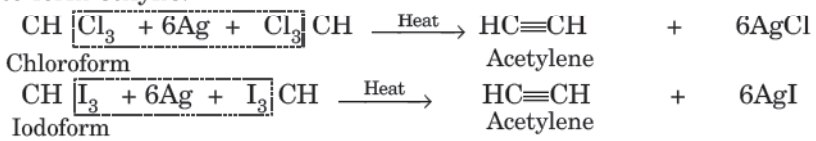
5. By electrolysis of aqueous solution of potassium salt of fumaric acid. Acetylene is prepared by the electrolysis of aqueous solution of potassium salt of maleic acid or fumaric acid.



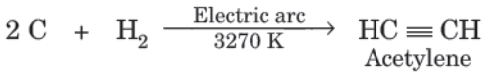
This reacton is called Kolbe's **electrolysis reaction.** It is believed to occur as :



6. By dehalogenation of haloforms. Chloroform and iodoform on heating with silver powder undergo dehalogenation to form ethyne.



7. Synthesis from carbon and hydrogen. Acetylene can be prepared by passing a stream of hydrogen through electric arc struck between carbon electrodes at 3270 K.



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SUM UP

Electrolysis reactions for the preparation of alkane, alkene and alkyne.

- *Electrolysis of aqueous solution of sodium or potassium salt of acetic acid gives ethane* **(alkane)**

$$\underset{\text{Potassium acetate}}{\begin{matrix}CH_3COOK\\+\\CH_3COOK\end{matrix}} \xrightarrow[(aq)]{\text{Electrolysis}} \underset{\text{Ethane}}{\begin{matrix}CH_3\\|\\CH_3\end{matrix}}$$

- *Electrolysis of aqueous solution of potassium salt of succinic acid gives ethylene* (**alkene**)

$$\underset{\text{Potassium succinate}}{\begin{matrix}CH_2COOK\\|\\CH_2COOK\end{matrix}} \xrightarrow[(aq)]{\text{Electrolysis}} \underset{\text{Ethylene}}{\begin{matrix}CH_2\\\|\\CH_2\end{matrix}}$$

- *Electrolysis of aqueous solution of potassium salt of fumaric acid gives acetylene* (**alkyne**)

$$\underset{\text{Pot. fumarate}}{\begin{matrix}CHCOOK\\\|\\CHCOOK\end{matrix}} \xrightarrow{\text{Electrolysis}} \underset{\text{Acetylene}}{\begin{matrix}CH\\\|\|\\CH\end{matrix}}$$

Properties of Alkynes

Alkynes contain carbon-carbon triple bond (C ≡ C) in their molecules. Alkynes resemble alkenes in most of their characteristics.

Physical Properties

1. Physical state and smell. The first three members (ethyne, propyne and butyne) of the family are gases at room temperature, the next eight are liquids while the higher ones are solids. All alkynes are colourless. However, ethyne has characteristic odour of garlic smell.

2. Solubility. Alkynes are weakly polar in nature. They are lighter than water and immisible with water but are soluble in organic solvents such as *petroleum ether, carbon tetrachloride, benzene, etc.*

3. Melting and boiling points. The melting and boiling points of the members of the family are slightly higher as compared to those of the corresponding members of the alkane and alkene families. This is due to the fact that the alkynes have linear structure and therefore, their molecules are more closely packed in space as compared to the alkanes and alkenes. The magnitude of attractive forces among them are higher and therefore, the melting and boiling points are also higher. The melting and boiling points increase with increase in molecular mass of the alkynes.

Hydrocarbon	Ethane	Ethene	Ethyne
m.p. (K)	101	104	191
b.p. (K)	184.5	171	198

Chemical Properties

The alkynes have at least one triple bond (— C ≡ C —) in them, therefore, they are quite reactive chemically. They readily take part in addition reactions and can also be easily oxidised. A few important chemical characteristics are discussed below :

1. Acidic character of Alkynes

Acetylene and other terminal alkynes (1-alkynes) are *weakly* acidic in character. They react with strong bases like sodium metal at 475K or sodamide, $NaNH_2$ (in liquid ammonia at 196K) to form sodium acetylide derivatives known as **acetylides** or **alkynides** with the liberation of dihydrogen gas.

$$H{-}C{\equiv}C{-}H + Na \longrightarrow \underset{\text{Monosodium ethynide}}{H{-}C{\equiv}C^-Na^+} + \tfrac{1}{2}H_2$$

$$H{-}C{\equiv}C^-Na^+ + Na \longrightarrow \underset{\text{Disodium ethynide}}{Na^+\,{}^-C{\equiv}C^-Na^+} + \tfrac{1}{2}H_2$$

$$\underset{\substack{\text{Ethyne}\\\text{(Acetylene)}}}{H{-}C{\equiv}C{-}H} + \underset{\text{Sodamide}}{NaNH_2} \longrightarrow \underset{\text{Monosodium ethynide}}{H{-}C{\equiv}C^-Na^+} + NH_3$$

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$$H-C\equiv C-H + \underset{\text{Sodamide}}{2NaNH_2} \longrightarrow \underset{\text{Disodium ethynide}}{Na^+\,^-C\equiv C^-Na^+} + 2NH_3$$

$$\underset{\text{(terminal alkyne)}}{R-C\equiv C-H} + \underset{\text{Sodamide}}{Na^+NH_2^-} \longrightarrow \underset{\text{Sodium alkynide}}{R-C\equiv C^-Na^+} + NH_3$$

These reactions have not been observed in case of **alkenes** and **alkanes** indicating that alkynes are acidic in nature in comparison to alkenes and alkanes.

Sodium alkynide is decomposed by water regenerating alkyne.

$$\underset{\text{Sodium alkynide}}{R-C\equiv C^-Na^+} + H_2O \longrightarrow \underset{\text{Alkyne}}{R-C\equiv CH} + NaOH$$

This shows that water is a stronger acid than alkynes and therefore, displaces alkyne from sodium alkynide.

e.g. $$\underset{\text{Monosodium acetylide}}{HC\equiv C^-Na^+} + H_2O \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + NaOH$$

Acetylides react with alkyl halides to give **higher alkynes.** For example,

$$HC\equiv CNa + \underset{\text{Methyl bromide}}{CH_3Br} \longrightarrow \underset{\text{Propyne}}{HC\equiv C-CH_3} + NaBr$$

The acetylenic hydrogen of alkynes can be replaced by copper (I) or silver (I) ions. They react with ammoniacal solutions of cuprous chloride $[Cu(NH_3)_2]^+OH^-$ and ammoniacal silver nitrate $[Ag(NH_3)_2]^+OH^-$ solution (called *Tollen's reagent)* to form the corresponding copper and silver alkynides.

$$\underset{\text{Acetylene}}{H-C\equiv C-H} + \underset{\text{Diamminecopper (I) hydroxide}}{2[Cu(NH_3)_2]^+OH^-} \longrightarrow \underset{\text{Dicopper acetylide (Red ppt)}}{CuC\equiv CCu} + 2H_2O + 4NH_3$$

$$\underset{\text{(terminal alkyne)}}{R-C\equiv CH} + [Cu(NH_3)_2]^+OH^- \longrightarrow \underset{\text{Monocopper alkynide (Red ppt)}}{R-C\equiv CCu} + H_2O + 2NH_3$$

$$\underset{\text{Acetylene}}{H-C\equiv C-H} + \underset{\text{Diammine silver (I) nitrate}}{2[Ag(NH_3)_2]^+OH^-} \xrightarrow{NH_4OH} \underset{\text{Disilver acetylide (White ppt.)}}{AgC\equiv CAg} + 2H_2O + 4NH_3$$

$$\underset{\text{(terminal alkyne)}}{R-C\equiv CH} + [Ag(NH_3)_2]^+OH^- \longrightarrow \underset{\text{Silver alkynide (White ppt)}}{R-C\equiv CAg} + H_2O + 2NH_3$$

Unlike alkali metal acetylides, copper and silver acetylides are not decomposed by water. However on treatment with dilute mineral acids, they regenerate original alkynes.

$$\underset{\text{Dicopper acetylide}}{CuC\equiv CCu} + 2HCl \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + 2CuCl$$

$$AgC\equiv CAg + 2HNO_3 \longrightarrow HC\equiv CH + 2AgNO_3$$

It may be noted that heavy metal acetylides are highly explosive when dry. Therefore, these should be destroyed while still wet by warming with nitric acid.

It may be noted that only the terminal alkynes (1-alkynes) react with ammoniacal solution of silver nitrate or cuprous chloride. Therefore, this reaction can be used to distinguish between 2-alkynes and 1-alkynes. 1-Alkynes will give this test while 2-alkynes will not give this test.

$$\underset{\text{But-1-yne}}{CH_3CH_2C\equiv CH} + [Ag(NH_3)_2]OH \longrightarrow \underset{\text{White ppt.}}{CH_3CH_2C\equiv CAg}$$

$$\underset{\text{But-2-yne}}{CH_3C\equiv CCH_3} + [Ag(NH_3)_2]OH \longrightarrow \textbf{No reaction}$$

Explanation for the acidic character of alkynes. The acidic character of 1-alkynes can be explained on the basis of *sp* hybridisation state of the carbon atoms in alkynes. We know that an electron in *s*-orbital is more tightly held than in a *p*-orbital because *s*-electrons are more closer to the nucleus. In *sp* hybridisation, *s*-character is more (50%) as compared to sp^2 (33%) or sp^3 (25%) hybrid orbitals. Due to very large *s*-character, the electrons in *sp* hybrid orbitals are held more tightly by the nucleus and are quite electronegative. Consequently, the electron pair of H — C≡ bond gets displaced more towards the carbon atom and helps in the release of a proton (H^+ ion).

$$R-C\equiv C\cdots\cdots H \qquad \text{(Cleavage of bond is easy)}$$

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The alkynes with triple bond in the non-terminal position do not show any acidic character as there is no hydrogen atom attached directly to the triple bonded carbon atom ($H_3C - C \equiv C - CH_3$).

Comparison of relative acidic strengths of alkanes, alkenes and alkynes. The alkynes are weakly acidic in nature while alkenes and alkanes do not show any acidic nature. This is due the fact that the carbon atoms of the double bond are sp^2 hybridised (33% *s*-character) while those involved in the single bond are sp^3 hybridised (25% *s*-character). Because of lesser *s*-character, these carbon atoms are much less electronegative than the carbon atoms taking part in the triple bond. Therefore, the release of H^+ ion from an alkene and alkane molecule is difficult and they do not show acidic character. The acidic character decreases as :

$HC \equiv CH$	>	$CH_2 = CH_2$	>	$CH_3 - CH_3$
$K_a \approx 10^{-25}$		$K_a \approx 10^{-35}$		$K_a \approx 10^{-40}$

The relative acidity of acetylene is more than that of ammonia but less than that of water.

$$H_2O > HC \equiv CH > NH_3$$

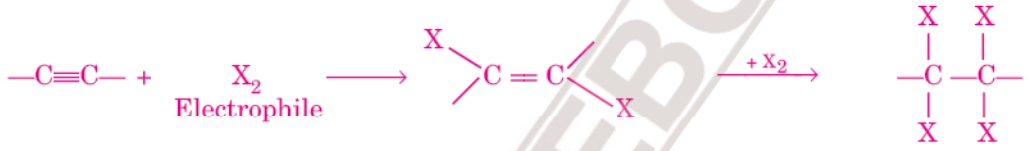
The acidity among alkynes is

$$HC \equiv CH > CH_3{-}C \equiv CH >> CH_3{-}C \equiv C{-}CH_3$$

It may be noted that hydrocarbons are weak acids as compared to water ($K_a \approx 10^{-14}$), alcohols ($K_a = 10^{-16}$ to 10^{-18}) and carboxylic acids ($K_a = 10^{-5}$).

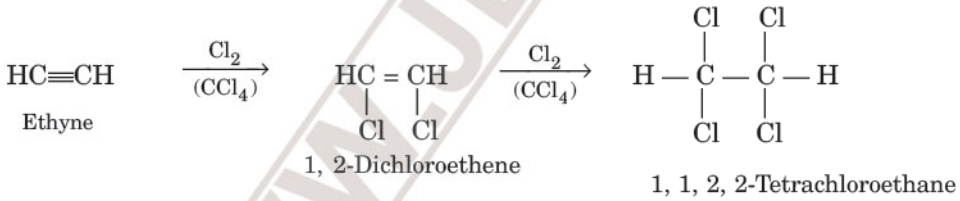
2. Addition Reactions

Like alkenes, alkynes undergo addition reactions due to their unsaturated nature. However, in alkynes, the addition occurs in two steps. In the first step, one molecule of the attacking reagent is added to the alkyne and its triple bond changes to a double bond. In the second step, a second molecule of the reagent is added which changes the double bond into a single bond and a saturated compound is obtained.

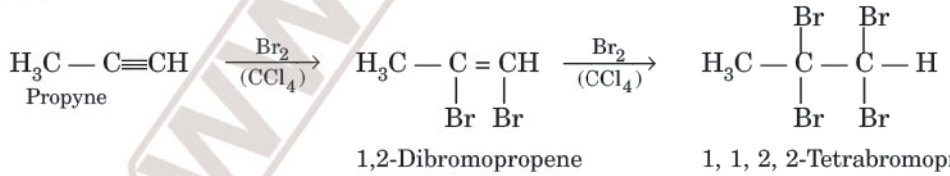


The alkenes formed by the addiction of X_2 to alkynes are generally ***trans*-isomers**. Some important electrophilic addition reactions are discussed below :

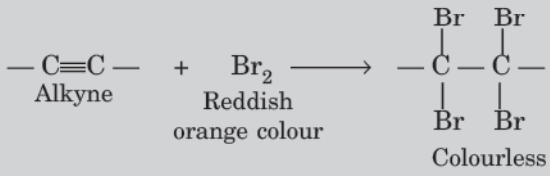
(*a*) Addition of halogens. Halogens add to alkynes in two steps forming a dihalide and then tetrahalide. For example,



1,1,2,2-tetrachloroethane is called westron. It is used as a solvent.



In case of addition of bromine, the reddish orange colour of solution of bromine in carbon tetrachloride gets discharged as in alkenes. Therefore, this can be used as a test for unsaturation in alkynes also. Thus, **the discharge of brown colour of bromine indicates the presence of unsaturation (alkenes or alkynes).**



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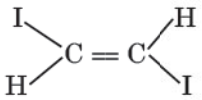
The reaction of alkynes with iodine is very slow reaction. It is believed to stop after the addition of one molecule of iodine to alkene stage as

$$HC \equiv CH + I_2 \xrightarrow{C_2H_5OH}$$

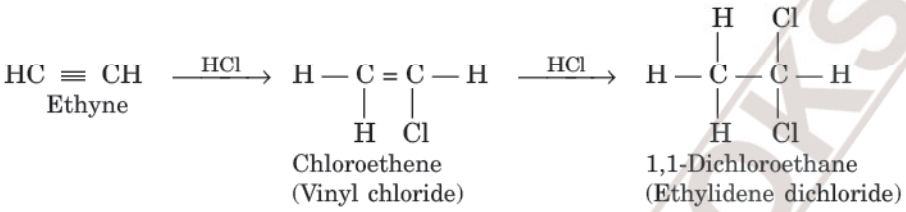


trans- 1, 2-diiodoethene

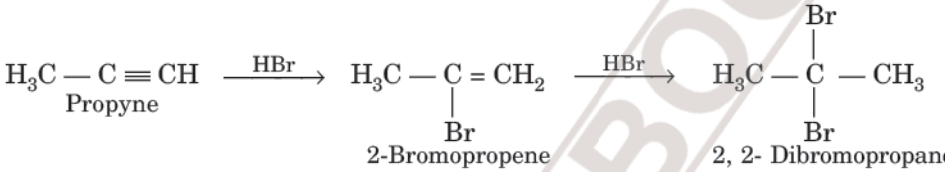
Thus, the **order of reactivity of halogens** towards alkynes is :

$$Cl_2 > Br_2 > I_2$$

(*b*) Addition of halogen acids. The addition of halogen acids (HCl, HBr and HI) also take place in two stages to form dihalogen derivatives. After one molecule of the acid has been added to a symmetrical alkyne, the product is an unsymmetrical derivative of alkene (vinyl halide). The further addition takes place in accordance with the Markovnikov rule to form *alkylidene dihalides (gem dihalides)* in which two halogens are attached to the same carbon atom. For example,



Ethyne → (HCl) Chloroethene (Vinyl chloride) → (HCl) 1,1-Dichloroethane (Ethylidene dichloride)



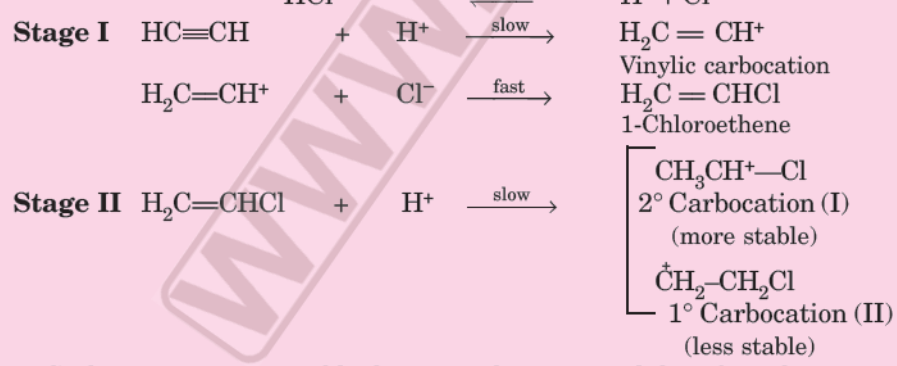
Propyne → (HBr) 2-Bromopropene → (HBr) 2, 2- Dibromopropane

It may be noted that peroxides have the same effect on the addition of hydrogen bromide to alkynes as they have on alkene.

The order of **reactivity** of halogen acids is HI > HBr > HCl > HF

Mechanism : Addition of halogen acids to alkynes.

The addition of halogen acids to alkynes is an electrophilic addition reaction similar to alkenes. It occurs in two stages and the path is decided by the stability of carbocation formed.



Stage I

$HCl \rightleftharpoons H^+ + Cl^-$

$HC{\equiv}CH + H^+ \xrightarrow{slow} H_2C = CH^+$ (Vinylic carbocation)

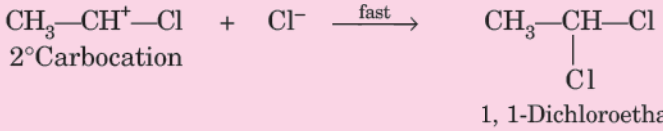
$H_2C{=}CH^+ + Cl^- \xrightarrow{fast} H_2C = CHCl$ (1-Chloroethene)

Stage II

$H_2C{=}CHCl + H^+ \xrightarrow{slow}$

- $CH_3CH^+{-}Cl$ — 2° Carbocation (I) (more stable)
- $\overset{+}{C}H_2{-}CH_2Cl$ — 1° Carbocation (II) (less stable)

2° Carbocation is more stable than 1° carbocation and therefore, the reaction occurs through carbocation (I) forming 1, 1-dichloroethane as



$CH_3{-}CH^+{-}Cl + Cl^- \xrightarrow{fast} CH_3{-}CH(Cl){-}Cl$

2°Carbocation → 1, 1-Dichloroethane

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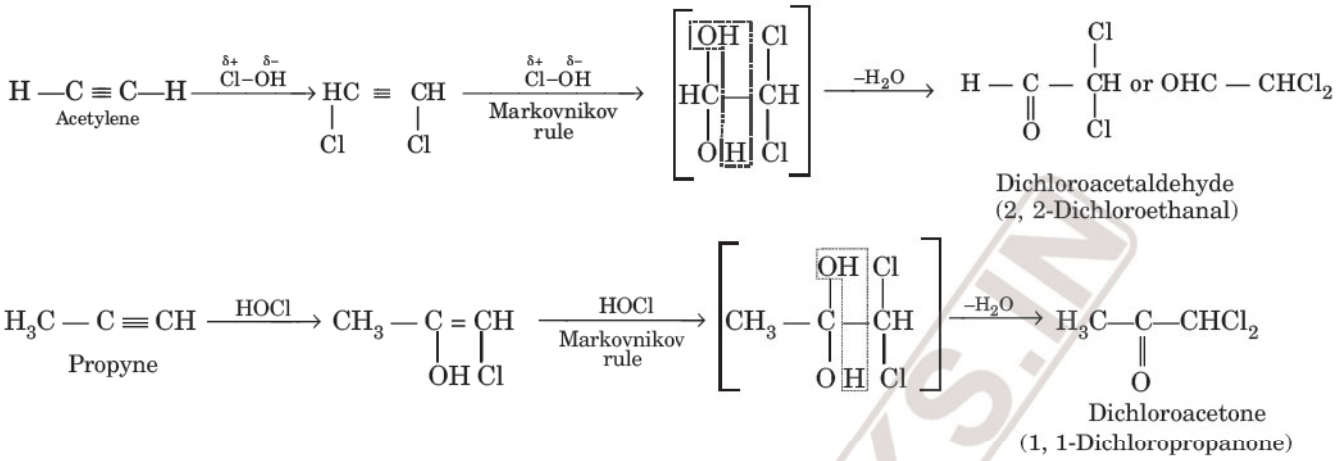
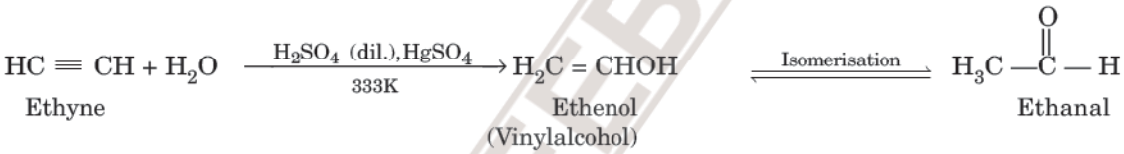
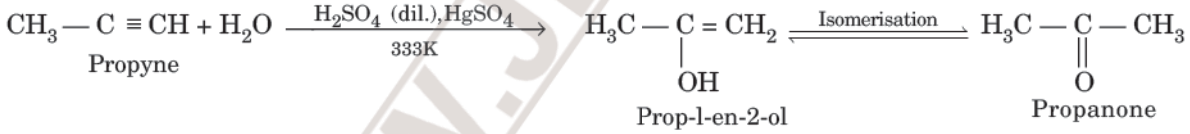
(*c*) Addition of hypohalous acid (HOX). Alkynes react with two molecules of hypohalous acids (HOCl or HOBr) or halogen Cl_2 or Br_2 in the presence of H_2O. For example,



(*d*) Addition of water (hydration of alkynes). Like alkanes and alkenes, alkynes are also immiscible and donot react with water. However, alkynes react with water in the presence of mercuric sulphate ($HgSO_4$) and sulphuric acid at 333 K. The products are carbonyl compounds (aldehydes and ketones). In this reaction, first enol is formed which contains a double bond (*ene*) and an alcoholic group (*ol*). But the enol formed is quite unstable in the acidic conditions. It isomerises to a more stable (*keto*) form as a result of rearrangement. For example :

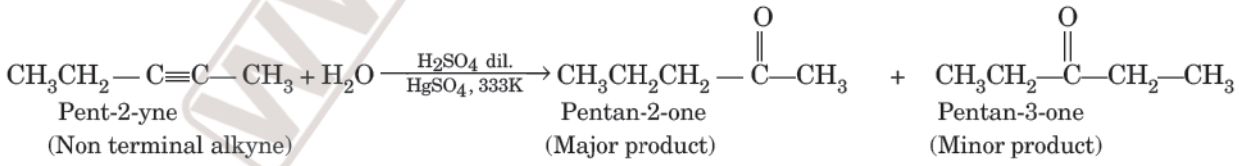


In case of unsymmetrical alkynes, the addition occurs in accordance with Morkovnikv's rule. For example,

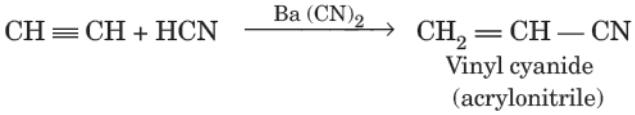


The rearrangement of enol form into keto form is called **tautomerism.**

However, if the unsymmetrical alkyne is non-terminal, a mixture of two isomeric ketones is obtained in which methyl ketone predominates. For example,



(*e*) Addition of hydrogen cyanide. Alkynes react with hydrogen cyanide (HCN) in the presence of barium cyanide catalyst. Acetylene gives vinyl cyanide or acrylonitrile which can be used to prepare synthetic fibre orlon.



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(*f*) Addition of alcohols and carboxylic acids. Ethyne adds a molecule of alcohol in the presence of alkali to give vinyl ether.

$$HC \equiv CH + CH_3OH \xrightarrow[393\text{-}453\ K]{KOH} \underset{\text{Methyl vinyl ether}}{H_3CO{-}HC = CH_2}$$

Similarly, alkynes add acids in the presence of a Lewis acid catalyst, Hg^{2+} ions to give vinyl esters. For example,

$$HC \equiv CH + CH_3COOH \xrightarrow{Hg^{2+},\ 353\,K} \underset{\text{Vinyl acetate}}{H_2C = CHOCOCH_3} \xrightarrow[CH_3COOH]{Hg^{2+}} \underset{\text{Ethylidene diacetate}}{CH_3{-}CH(OCOCH_3)_2}$$

Ethylidene diacetate on heating to 573–673 K gives acetaldehyde and acetic anhydride :

$$CH_3{-}CH(OCOCH_3)_2 \xrightarrow{573 - 673\,K} \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

(*g*) Addition of hydrogen (hydrogenation). Alkynes react readily with hydrogen in the presence of finely divided Ni, Pt or Pd as catalysts. The reaction is called *hydrogenation or reduction of alkynes*.

$$\underset{\text{Ethyne}}{HC \equiv CH} \xrightarrow[Pt\text{ or }Pd]{H_2,\ Ni\text{ or}} \underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow[Pt\text{ or }Pd]{H_2,\ Ni\text{ or}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

$$\underset{\text{Propyne}}{CH_3{-}C \equiv CH} \xrightarrow[or\ Pd]{H_2,\ Ni\text{ or }Pt} \underset{\text{Propene}}{CH_3CH = CH_2} \xrightarrow[or\ Pd]{H_2,\ Ni\text{ or }Pt} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

It may be noted that the hydrogenation can be controlled at the alkene stage only. This is possible by using a **Lindlar's catalyst** which is a mixture of palladium and barium sulphate poisoned by quinoline. It allows the hydrogenation of alkynes only to the alkene stage.

$$\underset{}{HC \equiv CH} \xrightarrow[\text{Quinoline}]{Pd,\ BaSO_4} \underset{\text{Ethene}}{CH_2 = CH_2}$$

(Lindlar's catalyst)

It may be noted that catalytic reduction of alkynes with hydrogen in the presence of **Lindlar's catalyst gives cis-alkenes**.

$$\underset{\text{But-2-yne}}{CH_3{-}C{\equiv}C{-}CH_3} \xrightarrow[\text{Quinoline}]{Pd,\ BaSO_4} \underset{\textit{cis}\text{ - But-2-ene}}{\overset{CH_3}{\overset{H}{>}C=C<}\overset{CH_3}{\underset{H}{<}}}$$

cis product using Lindlar's catalyst

However, chemical reduction (known as **Birch reduction**) of non-terminal alkynes with sodium (or lithium) in liquid NH_3 at 195–200K **gives trans alkenes**.

$$\underset{\text{But-2-yne}}{CH_3{-}C \equiv C{-}CH_3} \xrightarrow[196 - 200\,K]{Na\text{ in liq. }NH_3} \underset{\textit{trans}\text{ - But-2-ene}}{\overset{H}{\overset{CH_3}{>}C=C<}\overset{CH_3}{\underset{H}{<}}}$$

trans product using Birch reduction

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3. Oxidation

Alkynes can be oxidised under different conditions to give a variety of products.

(*a*) Combustion. When alkynes are burnt in air or oxygen, carbon dioxide and water are formed. The reaction is highly exothermic and a large amount of heat is produced.

$$\underset{\text{Ethyne}}{2HC{\equiv}CH} + 5O_2 \longrightarrow 4CO_2 + 2H_2O; \quad \Delta H = -1300\ kJ$$

Under normal conditions, acetylene burns with a luminous yellow sooty flame due to the presence of higher carbon content. However, with air or oxygen under high pressure, acetylene burns with a blue flame producing high temperature of the order of 3000 K. The heat produced during the combustion of acetylene can be used for welding purposes in the form of **oxy acetylene flame.**

(*b*) Oxidation with alkaline potassium permanganate

(*i*) With dilute cold $KMnO_4$ solution

Alkynes react with dilute cold alkaline $KMnO_4$ solution and form diketones or carboxylic acids depending upon the nature of alkyne.

In these reactions, ≡CH part of alkyne is oxidised to $-\overset{\overset{O}{\|}}{C}-OH$ group while RC≡ part is oxidised to $R-\overset{\overset{O}{\|}}{C}-$ part. For example,

$$\underset{\text{Propyne}}{CH_3C{\equiv}CH} + \underset{\text{Baeyer's reagent}}{KMnO_4} + H_2O \xrightarrow{298-303\ K} CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$

2-Oxopropanoic acid (Pyruvic acid)

$$\underset{\text{But-2-yne}}{CH_3-C{\equiv}C-CH_3} \xrightarrow[298-303\ K]{\text{dil. Alkaline } KMnO_4} CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$

Butane-2, 3-dione (Biacetyl)

Acetylene under these conditions gives oxalic acid.

$$\begin{matrix}CH\\ \|\\ CH\end{matrix} + 4\,[O] \xrightarrow[298-303K]{\text{Alk. } KMnO_4} \begin{matrix}COOH\\ |\\ COOH\end{matrix}$$

Ethane-1, 2-dioic acid
(Oxalic acid)

In the above reactions, the pink colour of alkaline $KMnO_4$ (Baeyer's reagent) gets discharged. Therefore, this reaction can be used as a test for alkynes.

(*ii*) With hot $KMnO_4$ solution

When alkynes are treated with hot $KMnO_4$ solution, the triple bond is completely broken leading to the formation of carboxylic acids and carbon dioxide depending upon the position of triple bond. The cleavage occurs at the site of triple bond.

$$\underset{\text{Propyne}}{CH_3C{\equiv}CH} \xrightarrow[373-383\ K]{\text{Alkaline } KMnO_4} \underset{\text{Ethanoic acid}}{CH_3COOH} + CO_2$$

In this case, ≡CH part of alkyne is oxidised to CO_2 and H_2O while RC≡ part is oxidised to RCOOH. For example,

$$\underset{\text{Ethyne}}{HC{\equiv}CH} \xrightarrow[373-383\ K]{\text{Alkaline } KMnO_4} 2CO_2 + H_2O$$

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$$CH_3CH_2C\equiv CH \xrightarrow[373\text{–}383\ K]{\text{Alkaline } KMnO_4} CH_3CH_2COOH + CO_2$$
But –1–yne — Propanoic acid

$$CH_3-C\equiv C-CH_3 \xrightarrow[373\text{–}383K]{\text{Alkaline } KMnO_4} 2CH_3COOH$$
But-2-yne — Ethanoic acid

$$CH_3CH_2C\equiv CCH_3 \xrightarrow[373\text{–}383\ K]{\text{Alkaline } KMnO_4} CH_3CH_2COOH + CH_3COOH$$
Pent–2–yne — Propanoic acid + Ethanoic acid

The above reactions in which triple bond is completely broken are called **degradation** or **cleavage reactions.** These can be used to locate the position of triple bond.

It may be remembered that
with **cold $KMnO_4$** (at 298-303 K)
$\equiv$CH part is oxidised to — COOH group
$\equiv$CR part is oxidised to R — C(=O) — group

with **acidic $KMnO_4$ at high temperature** (373-383 K)
$\equiv$CH part is oxidised to CO_2 and H_2O
$\equiv$CR part gets oxidised to RCOOH.
e.g.,

$CH_3CH_2C\equiv CH$ (But-1-yne)
- Acidic $KMnO_4$, 373–383 K → $CH_3CH_2COOH + CO_2 + H_2O$ (Propanoic acid)
- $KMnO_4$, 298–303K → $CH_3CH_2C(=O)-COOH$ (2-Ketobutanoic acid)

(*c*) Oxidation with ozone (Ozonolysis). The alkynes react with ozone to form ozonides. These ozonides on decomposition with zine dust and water or H_2/Pd (reductive cleavage) give dicarbonyl compounds.

$$CH_3-C\equiv CH \xrightarrow{O_3} CH_3-\underset{\displaystyle O-O}{\overset{O}{\overset{/\backslash}{C-CH}}} \xrightarrow[-ZnO]{Zn,\ H_2O} CH_3-\underset{O}{\overset{O}{\overset{\|}{C}}}-\underset{O}{\overset{O}{\overset{\|}{C}}}-H$$
Propyne — Propyne ozonide — 2-Oxopropanal

$$CH_3C\equiv CCH_3 \xrightarrow{O_3} CH_3-\underset{\displaystyle O-O}{\overset{O}{\overset{/\backslash}{C-C}}}-CH_3 \xrightarrow[-ZnO]{Zn,\ H_2O} CH_3-\underset{O}{\overset{O}{\overset{\|}{C}}}-\underset{O}{\overset{O}{\overset{\|}{C}}}-CH_3$$
But-2-yne — But-2-yne ozonide — Butane-2,3-dione

Ethyne gives glyoxal on ozonolysis.

$$CH\equiv CH + O_3 \longrightarrow HC\underset{\displaystyle O-O}{\overset{O}{\overset{/\backslash}{-CH}}} \xrightarrow[-ZnO]{Zn,\ H_2O} H-\underset{O}{\overset{O}{\overset{\|}{C}}}-\underset{O}{\overset{O}{\overset{\|}{C}}}-H$$
Ethyne — 1, 2-Ethanedial (Glyoxal)

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4. Polymerisation Reactions

Alkynes have larger tendency to polymerize than alkenes and therefore undergo two types of polymerization reactions :

(a) Linear polymerisation

(*i*) Acetylene undergoes linear polymerisation under suitable conditions to form linear polymer **polyacetylene** or **polyethyne.** It is a high molecular mass conjugated diene containing repeating units of (CH═CH—CH═CH) and the polymer can be represented as $-(CH{=}CH{-}CH{=}CH-)_n$. Under special conditions, this polymer conducts electricity. Thin sheets of polyacetylene can be used as electrodes in batteries.

(*ii*) On passing acetylene through a solution of cuprous chloride and ammonium chloride at 343K, vinylacetylene and divinylacetylene are formed.

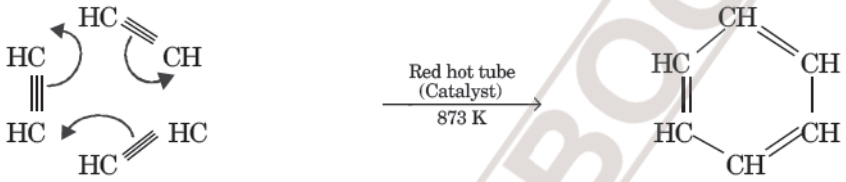
$$\underset{\text{Acetylene}}{2HC{\equiv}CH} \xrightarrow[343K]{Cu_2Cl_2,NH_4Cl} \underset{\text{Vinylacetylene}}{H{-}C{\equiv}C{-}CH{=}CH_2} \xrightarrow[Cu_2Cl_2/NH_4Cl]{CH{\equiv}CH} \underset{\text{Divinylacetylene}}{H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2}$$

Vinylacetylene is widely used in the manufacture of chloroprene which is a starting material for the synthetic rubber **neoprene**.

$$\underset{\text{Vinyl acetylene}}{CH_2{=}CH{-}C{\equiv}CH} + HCl \xrightarrow[\text{addition}]{\text{Markovnikov}} \underset{\text{Chloroprene}}{H_2C{=}CH{-}\overset{\overset{Cl}{|}}{C}{=}CH_2}$$

(b) Cyclic polymerisation. Alkynes on passing through red-hot iron tube at 873K, undergo cyclic polymerisation. For example,

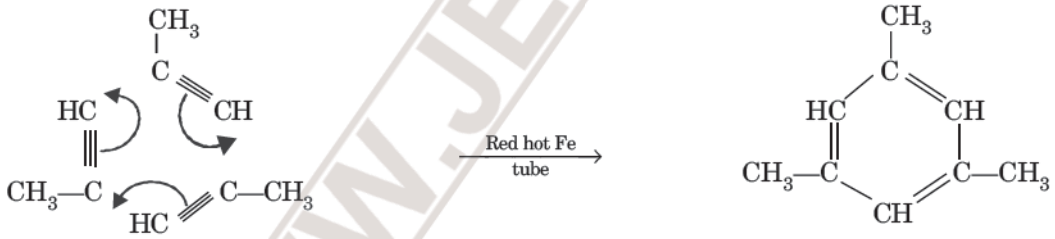
(*i*) When ethyne is passed through red hot tube at 873 K, three molecules of it polymerise to give benzene.



3 molecules of acetylene — Benzene

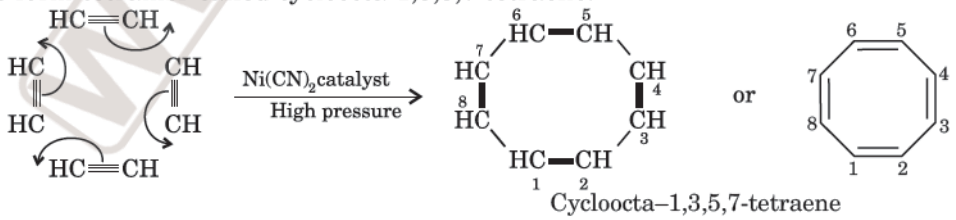
This is a best route for entering from aliphatic to aromatic compounds. Benzene can be used as a starting material for preparation of derivatives of benzene and other organic compounds.

Similarly, propyne trimerises under similar conditions to form mesitylene (1, 3, 5-trimethyl benzene).



1, 3, 5-Trimethylbenzene
(Mesitylene)

(*ii*) Four molecules of ethyne combine together in the presence of nickel cyanide as catalyst and under high pressure to form tetramer called cycloocta-1,3,5,7-tetraene.



Cycloocta–1,3,5,7-tetraene

5. Isomerization of alkynes

When alkynes are heated with sodamide ($NaNH_2$) in an inert solvent, such as kerosene oil or paraffin oil, they undergo isomerization *i.e.*, 2-alkynes isomerize to 1-alkynes. However, in the presence of alcoholic potash reverse isomerization is effected.

$$\underset{\text{But-2-yne}}{CH_3C{\equiv}C{-}CH_3} \underset{\text{alc}\cdot KOH}{\overset{NaNH_2 \text{ in inert solvent}}{\rightleftharpoons}} \underset{\text{But-1-yne}}{CH_3CH_2C{\equiv}CH}$$

$$\underset{\text{But-1-yne}}{CH_3CH_2C{\equiv}CH} \underset{\text{alc}\cdot KOH}{\overset{NaNH_2 \text{ in inert solvent}}{\rightleftharpoons}} \underset{\text{But-2-yne}}{CH_3C{\equiv}C{-}CH_3}$$

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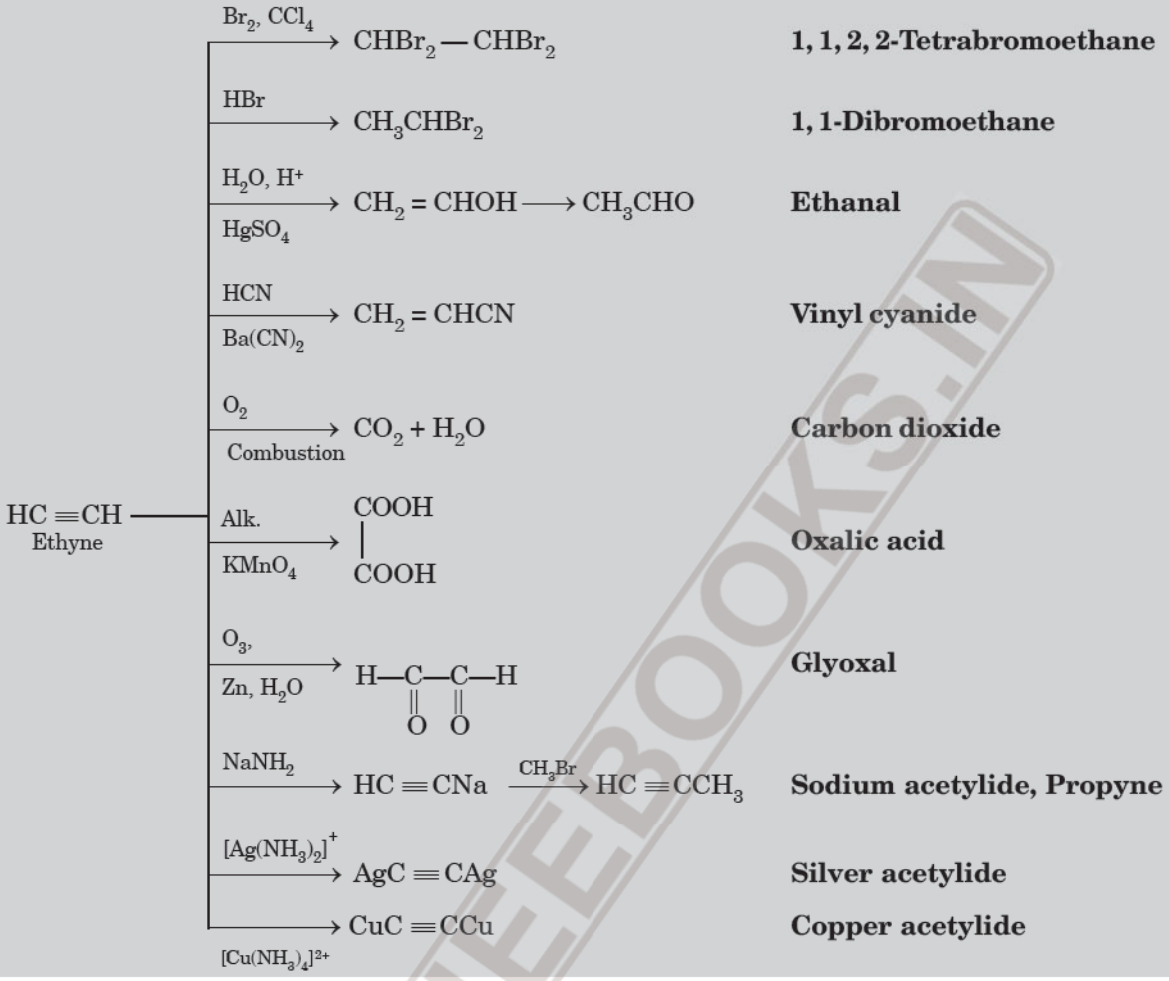
Summary of Reactions of Ethyne



SUM UP

Effect of Hybridisation on Bond Lengths, Bond dissociation enthalpies (or bond strengths) and Electronegativity

The bond length and bond strength of a bond depends upon the type of hybrid orbitals involved.

- **Bond length.** Since a *p*-orbital is bigger in size than an *s*-orbital of the same shell, therefore, as we go from sp^3 to sp^2 and to *sp*, the percentage of *p*-character decreases from 75% (in sp^3) to 66.7% (in sp^2) and to 50% (in *sp*). Accordingly, the size of hybrid orbitals decreases in the order : $sp^3 > sp^2 > sp$. As a larger orbital forms a larger bond, therefore, carbon-carbon bond length decreases in the order :

C (sp^3–sp^3)	>	C (sp^2–sp^2)	>	C (*sp*–*sp*)
154 pm		148 pm		138 pm
e.g., $H_3C—CH_3$		$H_2C=CH—CH=CH_2$		$CH\equiv C—C\equiv CH$

Bond length also decreases with an increase in the multiplicity of the bond (or bond order) because the sidewise overlap of *p*-orbitals to form π-bonds brings the two carbon atoms closer.

—C—C—	>C—C<	—C=C—
154 pm	134 pm	120 pm
e.g., $H_3C—CH_3$	$H_2C=CH_2$	$HC\equiv CH$

Similarly, a C—H bond may be formed by overlap of a sp^3, sp^2 or *sp*-orbital of carbon with an 1*s* orbital of hydrogen. As the size of the hybrid orbital decreases, the length of C—H bond also decreases. Consequently, a C—H bond formed with a carbon orbital to high *s*-character will be shorter than the one formed with a carbon of orbital of high *p*-character as:

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$C(sp^3)$–H	>	$C(sp^2)$–H	>	$C(sp)$–sp
111 pm		110 pm		108 pm
e.g., CH_4		$CH_2{=}{=}CH_2$		$CH{\equiv}C{-}H$

As discussed above, pi bonds are weaker than sigma bonds because during the formation of π-bonds. The extent of overlap is low. For example,

Carbon—Carbon (π bond)	Carbon—Carbon (σ bond)
284 kJ	348 kJ

However, a carbon-carbon double bond (in ethene) is stronger (681 kJ mol^{-1}) than a carbon-carbon single bond (348 in ethane). This is because a double bond consists of a strong σ-bond and a weak π-bond. Similarly, a carbon-carbon triple bond is stronger (823 kJ mol^{-1} in ethyne) than a carbon-carbon double bond because it consists of one σ-bond and two π-bonds.

In may be noted that bond length also increases with increase in size of the bonded atoms with C-orbital of the same type.

C—F	C—Cl	C—Br	C—I
142 pm	177 pm	191 pm	213 pm

- **Bond strength (or Bond enthalpy).** Bond strength increases with decrease in bond length. For example, for C—H bond,

$C(sp^3)$–H	<	$C(sp^2)$–H	<	$C(sp)$–H
436 kJ		443 kJ		507 kJ

Similarly, for C—C bond;

$C(sp^3)$–$C(sp^3)$	<	$C(sp^2)$–$C(sp^2)$	<	$C(sp$–$sp)$
348 kJ		383 kJ		433 kJ

- **Electronegativity.** The type of hybridisation also effects the electronegativity of the atom. The more the *s*-character of the hybrid orbital, more electronegative is the atom. Thus, a *sp*-hybridized carbon atom having 50% *s*-character is more electronegative than a sp^2-hybridized carbon atom with 33.33% *s*-character and sp^3 hybridized carbon with 25% *s*-character. This is mainly because *s*-orbital is more closer to the nucleus than a *p*-orbital and is more tightly hold by the nucleus and is, therefore, more electronegative.

SOLVED EXAMPLES

Example 21.

Write IUPAC names of the following ;

(*i*) $CH_2 = CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH = CH{-}CH = CH_2$ (*ii*) $CH \equiv C{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH = CH_2$

Solution:

(*i*) $\overset{7}{CH_2} = \overset{6}{CH}{-}\underset{\displaystyle \overset{5}{CH_3}}{\underset{|}{\overset{5}{CH}}}{-}\overset{4}{CH} = \overset{3}{CH}{-}\overset{2}{CH} = \overset{1}{CH_2}$

5-Methylhepta-1, 3, 6-triene

(*ii*) $\overset{1}{HC} \equiv \overset{2}{C}{-}\underset{\displaystyle \overset{5}{CH_3}}{\underset{|}{\overset{3}{CH}}}{-}\overset{4}{CH} = \overset{5}{CH_2}$

3-Methylpent-4-en-1-yne

Example 22.

Write structures of different isomers corresponding to the 5th member of alkynes series. Write IUPAC names of all the isomers and name the type of isomerism exhibited by different pairs of isomers.

Solution: 5th member of alkyne series has the molecular formula C_6H_{10}. The different isomers are :

(*i*) $\overset{1}{HC} \equiv \overset{2}{C}{-}\overset{3}{CH_2}{-}\overset{4}{CH_2}{-}\overset{5}{CH_2}{-}\overset{6}{CH_3}$ Hex-1-yne

(*ii*) $\overset{1}{CH_3}{-}\overset{2}{C} \equiv \overset{3}{C}{-}\overset{4}{CH_2}{-}\overset{5}{CH_2}{-}\overset{6}{CH_3}$ Hex-2-yne

(*iii*) $\overset{1}{CH_3}{-}\overset{2}{CH_2}{-}\overset{3}{C} \equiv \overset{4}{C}{-}\overset{5}{CH_2}{-}\overset{6}{CH_3}$ Hex-3-yne

(*iv*) $\overset{1}{HC} \equiv \overset{2}{C}{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{3}{CH}}}{-}\overset{4}{CH_2}{-}\overset{5}{CH_3}$ 3-Methylpent-1-yne

(*v*) $\overset{1}{HC} \equiv \overset{2}{C}{-}\overset{3}{CH_2}{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{4}{CH}}}{-}\overset{5}{CH_3}$ 4-Methylpent-1-yne

(*vi*) $\overset{1}{CH_3}{-}\overset{2}{C} \equiv \overset{3}{C}{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{4}{CH}}}{-}\overset{5}{CH_3}$ 4-Methylpent-2-yne

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(*vii*) $HC \equiv C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$ 3,3-Dimethylbut-1-yne

These represent position and chain isomerism shown by different pairs.

Example 23.

How would you separate propene from propyne ?

Solution: Pass the mixture through ammoniacal silver nitrate solution. Propyne will precipitate out as silver propynide and propene will pass unchanged.

$$H_3C-C \equiv CH + Ag^+ \longrightarrow \underset{\text{Precipitate}}{H_3C - C \equiv C^- Ag^+}$$

$$H_3C-CH = CH_2 + Ag^+ \longrightarrow \text{No reaction}$$

Example 24.

How would you carry out the following conversions ?

(*a*) $H_3CCH_2CH = CH_2 \longrightarrow H_3C-CH_2CH_2CH_2OH$

(*b*) $H_3C\,CH_2-CH = CH_2 \longrightarrow H_3C-CH_2-CH(OH)CH_2OH$

(*c*) $H_3CC \equiv CH \longrightarrow H_3C\,COCH_3$

(*d*) $Br_2\,CHCHBr_2 \longrightarrow HC \equiv CH$

Solution: (*a*) $H_3CCH_2CH = CH_2 \xrightarrow{B_2H_6,\ H_2O_2,\ OH^-} CH_3CH_2CH_2OH$

(*b*) $H_3C\,CH_2CH = CH_2 \xrightarrow{\text{Alk. } KMnO_4} H_3C-CH_2-\underset{\displaystyle OH}{\overset{|}{CH}}-\underset{\displaystyle OH}{\overset{|}{CH_2}}$

(*c*) $H_3CC \equiv CH \xrightarrow[Hg^{2+}]{H_2SO_4} \underset{\displaystyle OH}{\overset{|}{CH_3CH}} = CH_2 \xrightarrow{\text{Rearrangement}} CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3$

(*d*) $Br_2CHCHBr_2 \xrightarrow{Zn} HC \equiv CH$

Practice Problems

23. How will you prepare acetaldehyde from acetylene ?

24. Which of the following alkynes react with sodium in liquid ammonia ?
(*i*) Propyne (*ii*) But-2-yne (*iii*) Pent-3-yne (*iv*) Hex-1-yne

25. Name the process which may be used to locate the position of a triple bond.

26. Which of the following is most acidic
(*i*) Butane (*ii*) But-1-ene (*iii*) But-1-yne (*iv*) But-2-yne ?

27. What happens when water is dropped on calcium carbide ?

28. Name the reagent 'X' in the reaction :

$$\text{1, 2-Dibromoethane} \xrightarrow{X} \text{Acetylene}$$

29. Write chemical equation for the combustion of hexyne.

Answers to Practice Problems

23. $HC \equiv CH \xrightarrow[HgSO_4]{H^+,\ H_2O} H_2C = CHOH \rightleftharpoons CH_3CHO$

24. (*i*) and (*iv*)

25. Ozonolysis

26. (*iii*)

27. Acetylene is formed.

28. alc. KOH

29. $C_6H_{10}(g) + \frac{17}{2}O_2(g) \xrightarrow{\text{Heat}} 6CO_2(g) + 5H_2O(g)$

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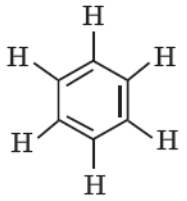
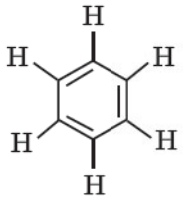
CHEMISTRY OF AROMATIC HYDROCARBONS

ARENES OR AROMATIC HYDROCARBONS

The parent members of the family is benzene having the molecular formula C_6H_6. It has hexagonal ring of six carbon atoms with three double bonds in alternate positions. It has a resonance stability and the structure may be represented as shown in (*c*).



(*a*)

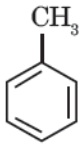


(*b*)

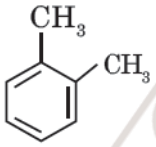
(*c*)

Most of these compounds possess pleasant odour (Greek *aroma* meaning pleasant smelling) and therefore, these compounds were named as **aromatic compounds.** Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids.** Some examples of arenes are :

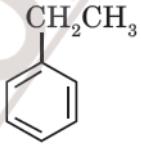
Benzene



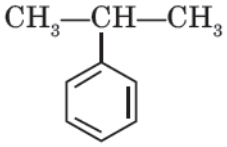
Toluene
(or Methyl benzene)



1, 2-Dimethylbenzene
(o-xylene)

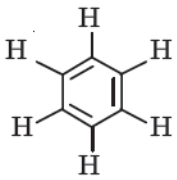


Ethylbenzene

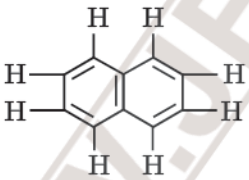


Isopropylbenzene
(cumene)

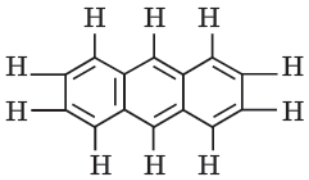
Monocyclic arenes like benzene (C_6H_6) have the general formula C_nH_{2n-6} and bicyclic arenes like naphthalene ($C_{10}H_8$) have the general formula C_nH_{2n-12}. In general an arene with '*m*' rings has the formula C_nH_{2n-6m}. The structures of monocyclic, bicyclic and tricyclic rings are given below :



Benzene

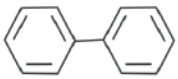


Naphthalene

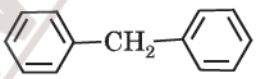


Anthracene

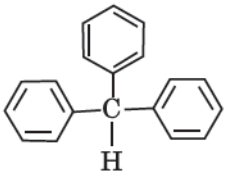
Some arenes may contain two or more isolated rings. For example,



Diphenyl or Biphenyl



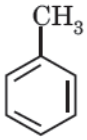
Diphenylmethane



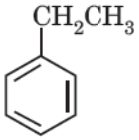
Triphenyl methane

NOMENCLATURE

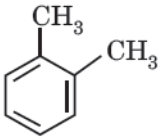
The nomenclature of aromatic hydrocarbons have already been discussed in the previous unit. Some common examples are :



Toluene



Ethylbenzene



1,2-Dimethylbenzene
(*o*-Xylene)

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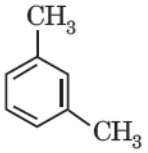
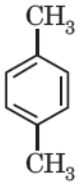
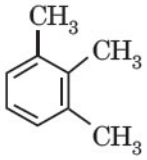


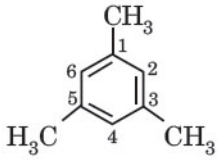
1,3-Dimethylbenzene
(*m*-Xylene)



1,4-Dimethylbenzene
(*p*-Xylene)



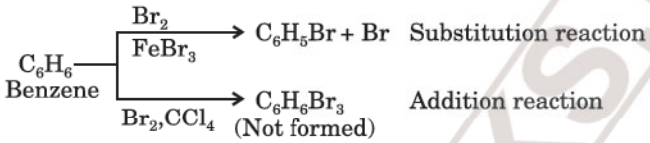
1, 2, 3-Trimethylbenzene



1, 3, 5-Trimethylbenzene
(Mesitylene)

STABILITY AND STRUCTURE OF BENZENE

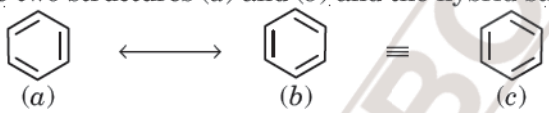
According to the structures, arenes are expected to be unsaturated and highly reactive in nature. However, they are stable. Because of unsaturated nature, benzene is expected to undergo only addition reactions like alkenes and alkynes. However, it does undergo addition reactions but it mainly undergoes substitution reactions in contrast to unsaturated hydrocarbons.



The stability of benzene is explained on the basis of resonance as well as its orbital structure.

Resonance in Benzene

The stability of benzene can be explained on the basis of concept of resonance. Kekule in 1865 gave a ring structure for benzene in which the positions of the three double bonds are not fixed. He suggested that the double bonds keep on changing their positions and this is called *resonance.* According to Kekule, benzene is a resonance hybrid of the two structures (*a*) and (*b*) and the hybrid structure may be represented as (*c*).



(*a*) (*b*) (*c*)

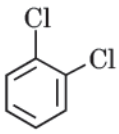
Kekule structures of benzene Resonance hybrid

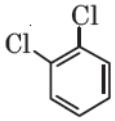
The resonance structure of benzene is **supported** by the following facts :

(*i*) The carbon-carbon bond length in benzene is 139 pm which is intermediate between bond lengths for C—C bond (154 pm) and C = C bond (134 pm) and the value is the same for all the bonds.

(*ii*) Due to resonance the π-electron charge in benzene gets distributed over greater area *i.e.,* it gets delocalised. As a result of delocalisation the energy of the resonance hybrid decreases as compared to contributing structures by about 50 kJ mol^{-1}. The decrease in energy is called **resonance energy.** Therefore, it is stabilised and behaves as a saturated hydrocarbon.

(*iii*) If the positions of double bonds are fixed, we expect two isomers of 1,2-dichlorobenzene as shown below (one having Cl atoms attached to C—C bond and the other having Cl atoms attached to C = C bond) :



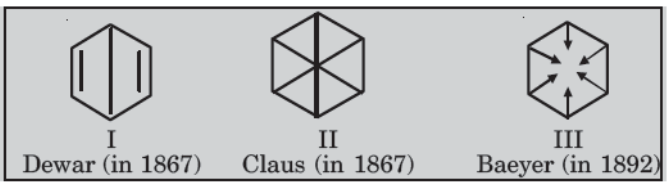


However, there is only one compound which can be explained only on the basis of equal type of bonds between the two carbon atoms. This supported the Kekule's proposed structure in which the double bonds in benzene are continuously oscillating back and forth between two adjacent positions. Since positions of double bonds are not fixed, only one product is formed.

Same product

This structure was also known as Kekule's dynamic formula in which he proposed dynamic equilibrium between two structures.

Though Kekule formula for benzene was accepted, many alternative structures have also been proposed from time to time by different workers. Some of these (I–III) are given :



I Dewar (in 1867) II Claus (in 1867) III Baeyer (in 1892)

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Modern Concept : Orbital Structure of Benzene

According to the orbital concept, each carbon atom in benzene is sp^2-hybridised and one orbital remains unhybridised. Out of the three hybrid orbitals, two overlap axially with the orbitals of the neighbouring carbon atoms on both sides to form σ-bonds. The third hybridised orbital of the carbon atom overlaps with the half-filled orbital of the hydrogen atom resulting in C—H bonds. Thus, benzene has a planar structure with bond angle of 120° each (Fig. 22).

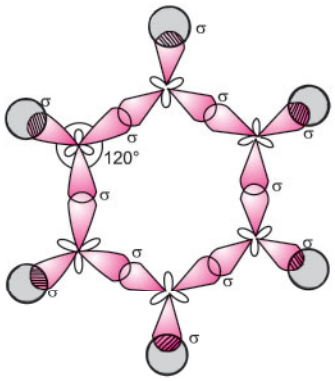

Fig. 22. Overlap of the hybridised orbitals of carbon to form σ-bonds.

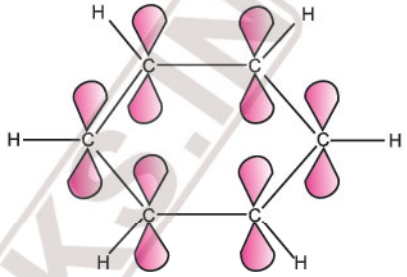

Fig. 23. Unhybridised 2*p*-orbital on each carbon atom.

There is still one unhybridised 2*p*-orbital left on each carbon atom as shown in Fig. 23. Each one of these orbitals can overlap sidewise with similar orbital of the carbon atoms on either sides to form two sets of π-bonds [Figs. 24 (*a*) and 24 (*b*)]. The resultant π-orbital cloud is spread over all the six carbon atoms and has been shown in Fig. 24 (*c*). As a result, there are two continuous rings of π-electron clouds, one above and the other below the plane of the carbon atoms as shown in Fig. 25.

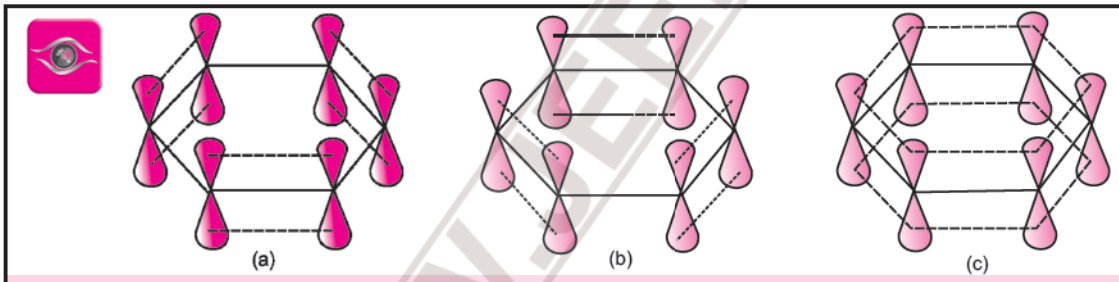

Fig. 24. Sidewise overlap of the unhybridised orbitals.

Therefore, benzene is a **flat molecule** in which the six carbon atoms are arranged at the corners of a hexagon. The π-electron charge in benzene is not confined to space between two carbon atoms as in ethylene, but is spread over a greater area. This is known as the **delocalisation** of the electron charge. This delocalisation results in the stronger bonds than the normal π-bonds and accounts for the stability of the molecule.

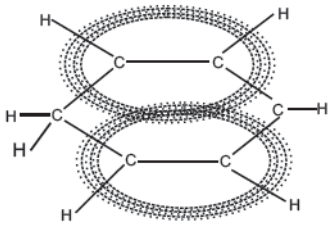

Fig. 25. π-electron clouds; one lying above and the other below the plane of carbon atoms.

Stability of benzene and enthalpy of hydrogenation

Benzene does not undergo addition reactions readily but it undergo substitution reactions like nitration, sulphonation, halogenation, etc. This shows that benzene is more stable than the hypothetical cyclohexatriene molecule. This unusal stability of benzene which had been puzzling the chemists for more than fifty years could only be explained on the basis of resonance concept. This has been proved by the fact that the enthalpies of hydrogenation and combustion of benzene are lower than expected on the basis of cyclohexatriene.

Enthalpy of hydrogenation is the amount of enthalpy change when one mole of an unsaturated hydrocarbon is hydrogenated. It has been experimentally observed that enthalpy of hydrogenation for

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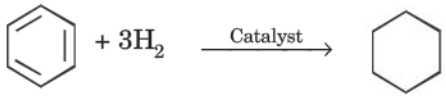
disubstituted alkenes, R—CH=CH–R varies between 117–125 kJ mol^{-1}. For example, the enthalpy of hydrogenation of cyclohexene is found to be 119.5 kJ mol^{-1}.

Cyclohexene Cyclohexane $\Delta H = -119.5$ kJ mol^{-1}

If the benzene contains three double bonds which do not interact (as in case of cyclohexatriene) then its enthalpy of hydrogenation should have been three times the enthalpy of hydrogenation of cyclohexene.

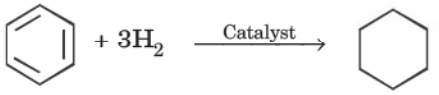
Enthalpy of hydrogenation expected for cyclohexatriene :



Cyclohexatriene Cyclohexane $\Delta H = -119.5 \times 3$

$= -358.5$ kJ mol^{-1}

However, the experimental value of enthalpy of hydrogenation of benzene is –208.1 kJ mol^{-1}



Benzene Cyclohexane $\Delta H = -208.1$ kJ mol^{-1}

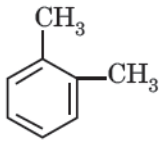
Thus, the actual molecule of benzene is more stable than hypothetical cyclohexatriene molecule by an amount equal to :

$$358.5 - 208.1 = 150.4 \text{ kJ mol}^{-1}$$

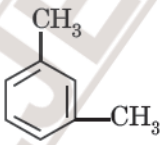
This is called **resonance energy.** Thus, resonance energy for benzene is 150.4 kJ mol^{-1}. This can also be confirmed by enthalpy of combustion data.

ISOMERISM IN ARENES

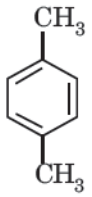
Arenes exhibit position isomerism. Monosubstituted benzenes do not show any isomerism because all the six hydrogen atoms attached to the carbon atoms are identical. The disubstituted arenes exhibit position isomerism. For example, there are three disubstituted benzenes namely 1,2 (or *ortho*), 1,3 (or *meta*) and 1,4 (or para) isomers as shown below :



1,2 Dimethylbenzene
(*ortho*-Xylene)

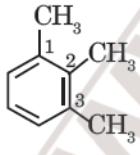


1,3-Dimethylbenzene
(*meta*-Xylene)

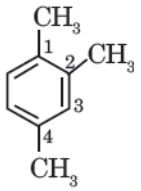


1,4-Dimethylbenzene
(*para*-Xylene)

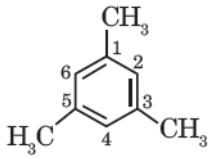
Similarly, three position isomers of trimethylbenzene are :



1,2,3-Trimethylbenzene

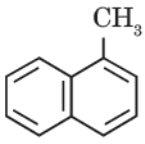


1,2,4-Trimethylbenzene

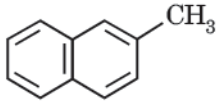


1,3,5-Trimethylbenzene
(Mesitylene)

In the case of naphthalene, even monosubstituted compounds exhibit isomers as in 1-methyl and 2-methyl naphthalene.



1-Methylnaphthalene
(α-Methylnaphthalene)



2-Methylnaphthalene
(β-Methylnaphthalene)

With higher arenes, the number of possible position isomers also increases.

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AROMATICITY (HUCKEL RULE)

We have learnt that aromatic compounds are those which resemble benzene in chemical behaviour. These compounds contain alternate double and single bonds in a cyclic structure. They undergo substitution reactions rather than addition reactions. This characteristic behaviour is called **aromatic character** or **aromaticity.**

Criteria for Aromaticity

The modern theory of aromaticity was advanced by Eric Huckel in 1931. The aromaticity depends upon the electronic structure of the molecule. A polynuclear compound, heterocyclic rings or cyclic ions may be aromatic if these have a specific electronic structure.

The main essentials for aromaticity are :

1. Delocalisation. The molecule should contain a cyclic cloud of delocalized π electrons above and below the plane of the molecule,

2. Planarity. For the delocalisation of π-electrons the ring must be planar to allow cyclic overlap of *p*-orbitals. Therefore, for a molecule to be aromatic, the ring must be planar.

3. (4*n* + 2) π electrons. For aromaticity, the π-electron cloud must contain a total of (4*n* + 2) π electrons where *n* is an integer equal to 0, 1, 2, 3 ..... . This is also known as **Huckel rule**.

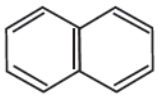
In a nutshell, ***for aromaticity, the molecule must be planar, cyclic system having delocalized (4n + 2)π electrons.***

This is known as **Huckel rule.**

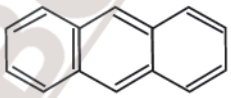
Thus, according to Huckel rule, the aromatic compounds have delocalized electron cloud of π electrons of 2 or 6 or 10 or 14 electrons.

For example, benzene (6π electrons), naphthalene (10π electrons) and anthracene (14π electrons) are aromatic compounds.

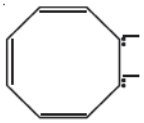
Benzene
6 π electrons
(*n* = 1)



Naphthalene
10 π electrons
(*n* = 2)

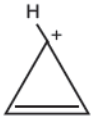


Anthracene
14 π electrons
(*n* = 3)

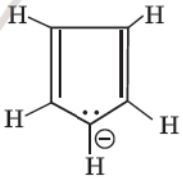


Cyclooctatetraenyl dianion
(**Aromatic :** planar, 10π electrons, *n* = 2)

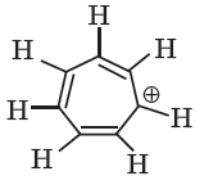
Similarly, cyclopropenyl cation, cyclopentadienyl anion and cycloheptatrienyl cation (tropylium ion) are also aromatic because these contain 6π electrons.



Cyclopropenyl cation
(**Aromatic :** Planar, 2π electrons, n = 0)

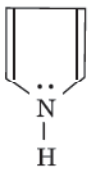


Cyclopentadienyl anion
(**Aromatic :** 6π electrons, *n* = 1)

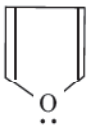


Cycloheptatrienyl cation
(Tropylium cation)
(**Aromatic :** Planar, 6π electrons, *n* = 1)

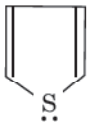
Heterocyclic compounds such as pyrrole, furan, thiophene and pyridine also behave as aromatic because all are planar and have a cyclic system of 6π-electrons which are delocalised over the ring.



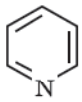
Pyrrole



Furan



Thiophene



Pyridine

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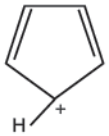
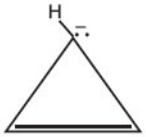
However, the following molecules or ions do not satisfy Huckel rule and are not aromatic.

Cyclopentadiene
4π electrons

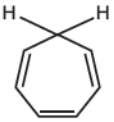


Cyclopentadienyl cation
4π electrons

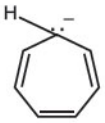
Cyclooctatetraene
8π electrons



Cyclopropenyl anion
4π electrons



Cycloheptatriene contains 6π electrons but π electrons are not spread over the entire ring

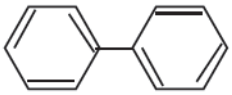
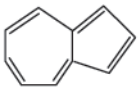


Cycloheptatrienyl anion
8π electrons

SOLVED EXAMPLES

Example 25.

Predict which of the following systems would be aromatic ?

(i) *(ii)*  *(iii)* *(iv)* 

Solution: Structures (*ii*) and (*iv*) are aromatic because they obey Huckel rule. Others are not aromatic because (*i*) contains 4π electrons (*iii*) contains 6π electrons but is not conjugated system due to a sp^3 carbon.

Example 26.

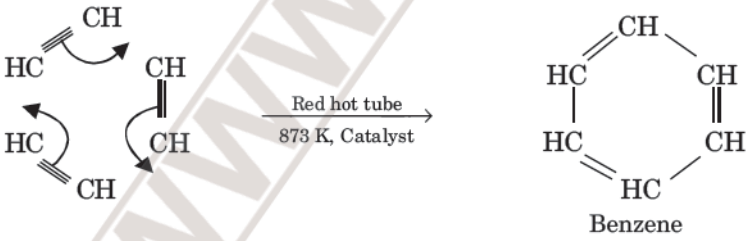
Is the following molecule aromatic or not ?

Solution: It is not aromatic because it is non-polar and contains 8π-electrons.

PREPARATION OF BENZENE AND ITS HOMOLOGUES

Benzene and its homologues can be prepared by the following methods :

1. From alkynes. Acetylene and other alkynes polymerise at high temperatures to give benzene and other arenes. For example, benzene was first synthesized by Berthelot by passing acetylene through red hot iron tube.

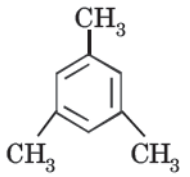


Benzene

or $3HC \equiv CH \xrightarrow[873\ K,\ Catalyst]{Red\ hot\ tube}$

Benzene

Similarly,

$3CH_3—C \equiv CH \xrightarrow[Catalyst]{873\ K}$ 

Propyne

1, 3, 5-Trimethyl benzene
(Mesitylene)

2. Decarboxylation of aromatic acids. Benzene is prepared in the laboratory by heating sodium benzoate with soda lime.

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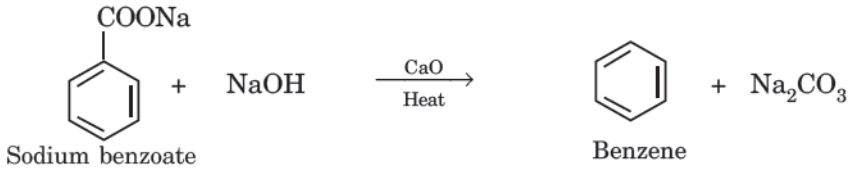
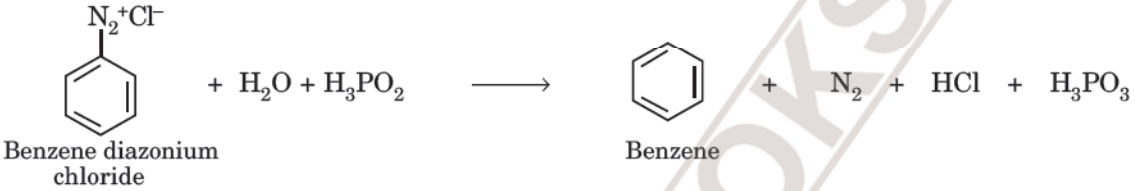


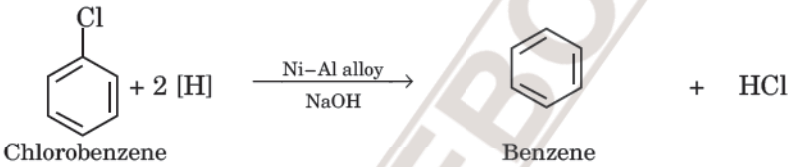
This reaction is called **decarboxylation reaction.**

3. Reduction of phenol. Benzene can be prepared by reduction of phenol by passing its vapours over heated zinc dust.

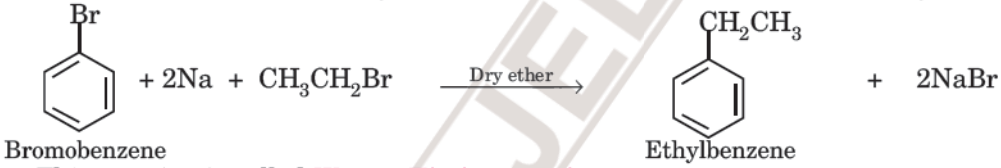
4. From diazonium salts. Benzene can be prepared from benzene diazonium chloride by reduction with hypophosphorus acid (H_3PO_2) in the presence of Cu(I) ions.



5. From aryl halides. Benzene can be prepared from chlorobenzene by reduction with Ni—Al alloy in the presence of sodium hydroxide.

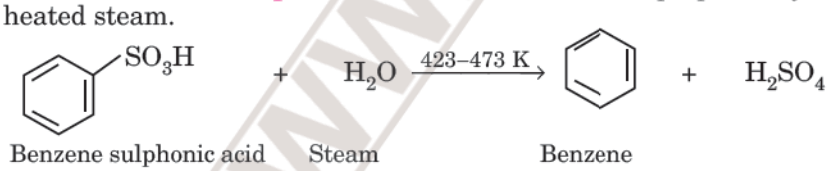


Arenes can also be obtained by the action of sodium metal on a mixture of aryl halide and alkyl halide in ether.

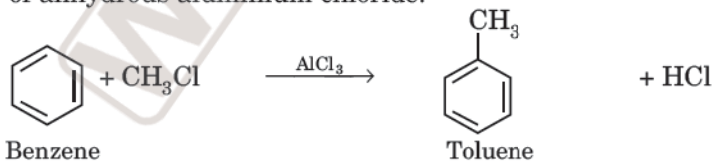


This reaction is called **Wurtz–Fittig reaction.**

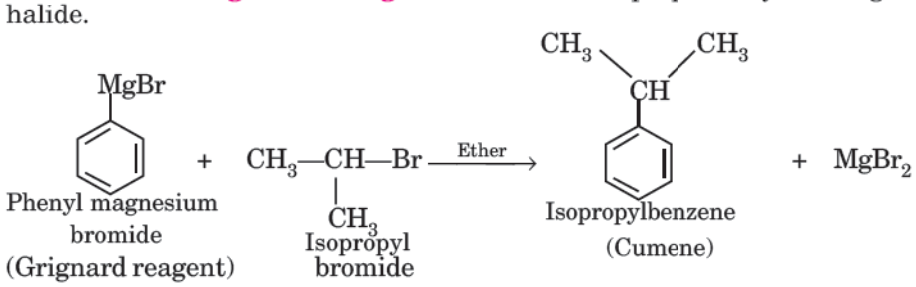
6. From benzene sulphonic acid. Benzene can be prepared by heating benzene sulphonic acid with super heated steam.



7. From Friedel Crafts reaction. Arenes can be obtained from benzene by treating with alkyl halide in the presence of anhydrous aluminium chloride.



8. From Grignard's reagent. Arenes can be prepared by reacting aromatic Grignard reagent with alkyl halide.



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PROPERTIES OF BENZENE AND ITS HOMOLOGUES

Physical Properties

(*i*) Benzene and its homologues containing upto eight carbon atoms are colourless liquids while the higher ones are solids with characteristic smell.

(*ii*) Aromatic hydrocarbons are immisible with water but are soluble in organic solvents.

(*iii*) They are inflammable and burn with sooty flame.

(*iv*) The melting and boiling points of aromatic hydrocarbons increase with increasing molecular mass. This is due to increase in magnitude of van der Waals' forces of attraction with increase in molecular size. Amongst isomeric arenes, (*i.e. o-*, *m-* and *p-* xylenes), the *p-* isomer has the highest melting point because it is most symmetrical.

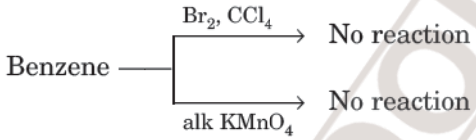
(*v*) They are toxic and carcinogenic in nature.

Chemical Properties

Arenes are expected to be quite reactive due to the presence of double bonds. However, benzene is quite stable and does not undergo common addition reactions undergone by alkenes. For example, benzene

(*i*) *does not decolourise bromine in* CCl_4

(*ii*) *does not decolourise alkaline* $KMnO_4$ *solution*.

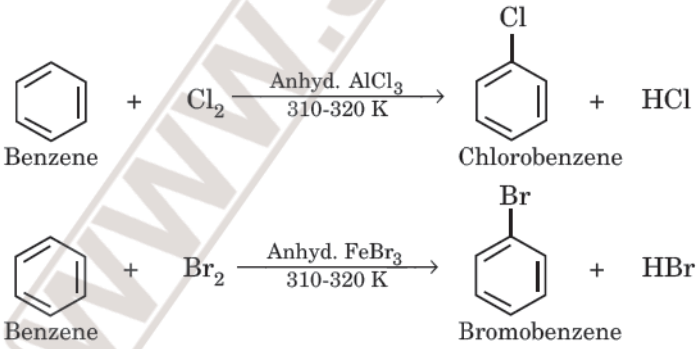


The stability of benzene is due to resonance. However, benzene and other arenes undergo following types of reactions :

1. *Substitution reactions*
2. *Addition reactions*
3. *Oxidation reactions*.

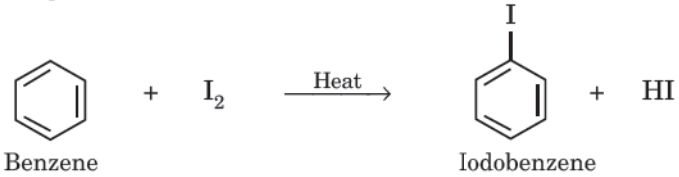
1. Substitution reactions. In these reactions, one or more hydrogen atoms in the benzene ring get replaced by other atoms or groups. For example :

(*a*) **Halogenation.** *The replacement of a hydrogen atom in the ring of an arene by a halogen atom* (*F*, *Cl*, *Br* or *I*) is called **halogenation**. The halogenation takes place in the presence of a **Lewis acid** such as ferric halide or aluminium halide which acts as *halogen carrier*. The chlorination and bromination occur at a temperature between 310 to 320 K.



The function of Lewis acids like $AlCl_3$, $FeCl_3$ *or* $FeBr_3$ *is to carry the halogen to aromatic hydrocarbons. Therefore, they are also called* **halogen carriers**.

Reaction with iodine is reversible because HI formed reduces iodo derivative back to benzene. Therefore, the reaction is carried out in the presence of an oxidising agent such as iodic acid (HIO_3) or nitric acid (HNO_3) or mercuric oxide (HgO).



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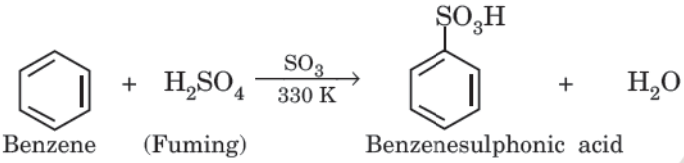
$$5HI + HIO_3 \xrightarrow{\text{Heat}} 3H_2O + 3I_2$$

$$6HI + 2HNO_3 \xrightarrow{\text{Heat}} 4H_2O + 2NO + 3I_2$$

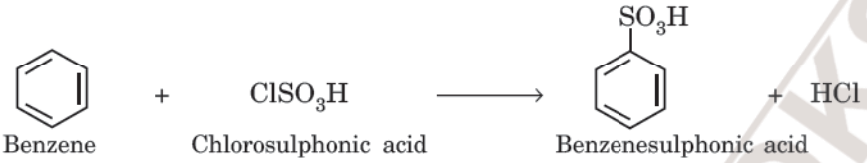
$$2HI + HgO \longrightarrow HgI_2 + H_2O$$

Fluorination is very fast and it is very difficult to control the reaction.

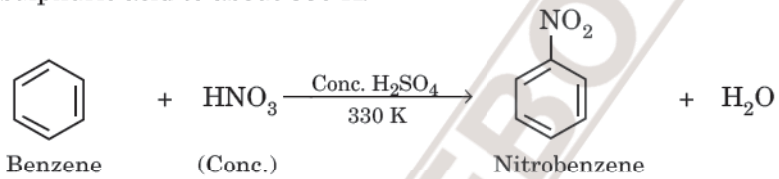
(*b*) **Sulphonation.** *The replacement of a hydrogen atom in the ring of an arene by a sulphonic acid* (– SO_3H) *group* is called **sulphonation.** It is carried out by heating benzene with fuming sulphuric acid or oleum (concentrated sulphuric acid containing dissolved sulphur trioxide). For example,



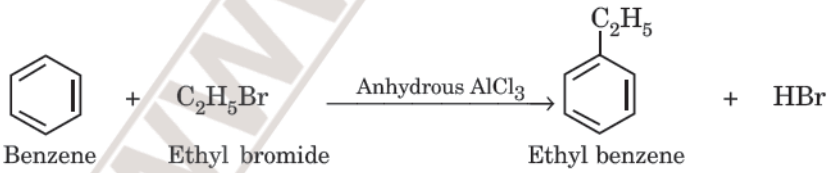
Sulphonation can also be carried by treating benzene with chlorosulphonic acid. For example,



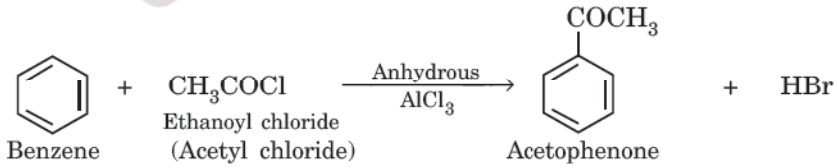
(*c*) Nitration. *The replacement of a hydrogen atom in the ring of an arene by a nitro (—NO_2) group* is called **nitration.** It is carried out by heating benzene with the nitrating mixture consisting of concentrated nitric acid and sulphuric acid to about 330 K.

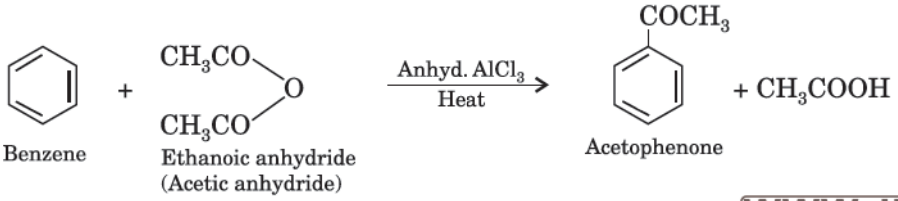


(*d*) Alkylation or Friedel-Crafts alkylation reaction. On treatment with an alkyl halide in the presence of anhydrous aluminium chloride, benzene forms an alkyl benzene. The reaction is also called **Friedel-Crafts alkylation reaction.** In this reaction, a hydrogen atom in the benzene ring is replaced by alkyl group. For example,



(e) Acylation or Friedel Crafts acylation reaction. On treatment with an acyl halide or acid anhydride in the presence of anhydrous $AlCl_3$ (Lewis acid), benzene forms acyl benzene. This reaction is called **Friedel Crafts acylation reaction.** For example,





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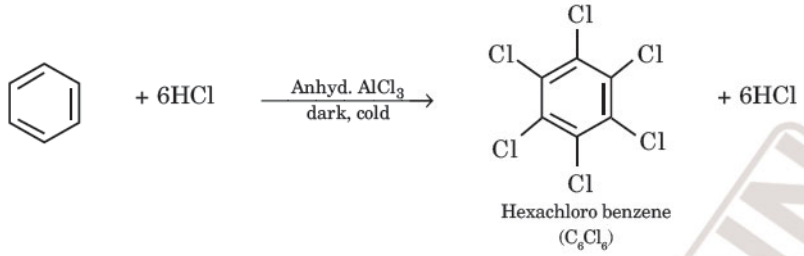
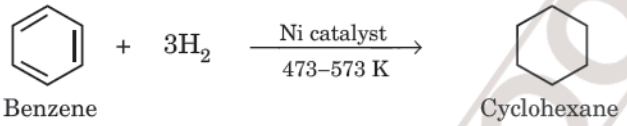
It may be noted that during electrophilic substitution reactions, if excess of electrophilic reagent is used, further substitution reaction may occur in which other hydrogen atoms of benzene ring may also be successively replaced by electrophile. For example, benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ in dark gives hexachlorobenzene (C_6Cl_6).



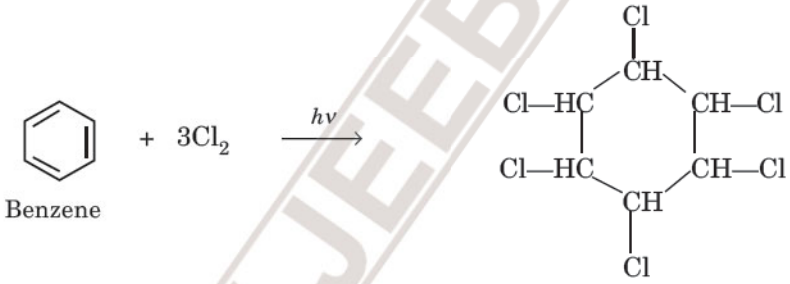
2. Addition Reactions

Benzene and its homologous also undergo some addition reactions characteristics of alkenes and alkynes. However, the reactions occur under more drastic conditions (higher temperature and pressure). This is due to extra stability of the delocalised π-electrons. For example,

(*a*) Addition of hydrogen (catalytic hydrogenation). Benzene reacts with hydrogen in the presence of a catalyst such as nickel or platinum at 473 to 573 K under pressure to form cyclohexane.

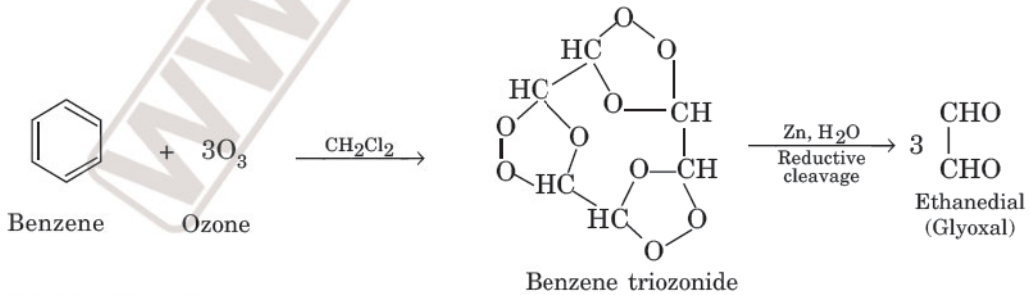


(*b*) Addition of halogens. Benzene reacts with chlorine or bromine in the presence of sunlight and absence of halogen carrier to form benzene hexachloride (BHC).



BHC is used as an insecticide. It is sold under the name **Gammexane** or **lindane.**

(*c*) Addition of ozone. Benzene reacts with ozone to form benzene triozonide which is decomposed by zinc dust and water to form glyoxal (ethanedial).



3. Oxidation Reactions

Arenes are quite stable and are not readily oxidised. Some of their oxidation reactions are :

(*a*) Combustion. On completely burning with oxygen, benzene gives carbon dioxide and water with the evolution of a large amount of energy.

$$2\,C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O; \qquad \Delta H = -6530\ kJ$$

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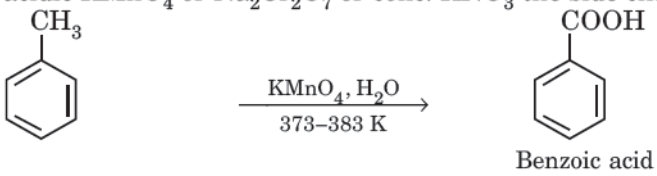
(*b*) Oxidation of benzene. Benzene on oxidation in the presence of vanadium pentoxide (V_2O_5) at 773 K gives maleic acid and maleic anhydride.

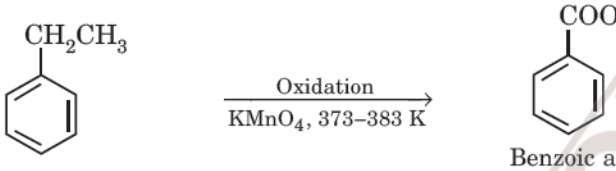
Benzene — Maleic acid — Maleic anhydride

(*c*) Oxidation of alkyl side chain. The alkyl side chain in arene can be oxidised by the following methods :

(*i*) With hot acidic $KMnO_4$ or $Na_2Cr_2O_7$ or conc. HNO_3 the side chain is oxidised to carboxylic acid group.

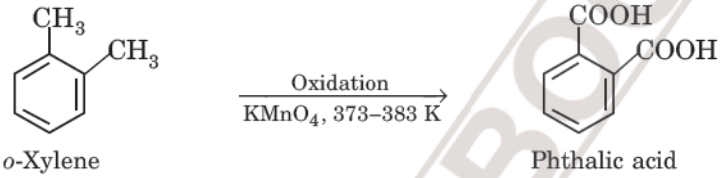


Benzoic acid

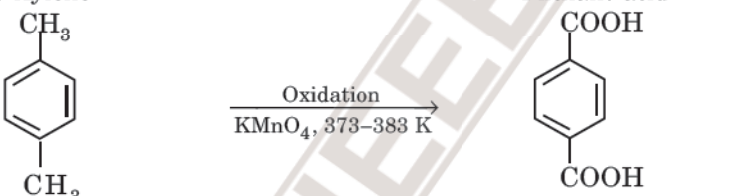


Benzoic acid

Xylenes on oxidation give dicarboxylic acids.



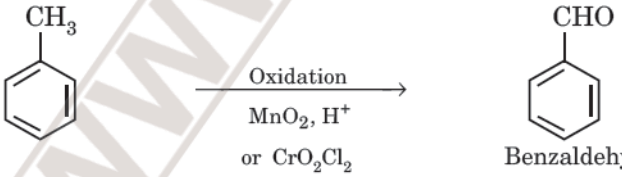
o-Xylene — Phthalic acid



p-Xylene — Terephthalic acid

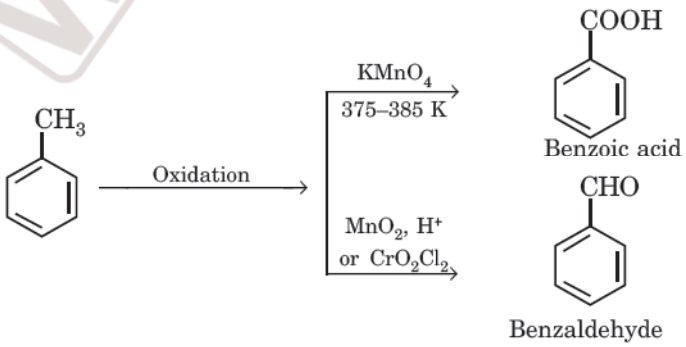
It may be noted that the side alkyl chain is oxidised to —COOH group irrespective of its length (—CH_3, —CH_2CH_3 or —$CH_2CH_2CH_3$).

(*ii*) With mild oxidising agents such as acidic manganese dioxide (MnO_2) or chromyl chloride (CrO_2Cl_2), the side chain is oxidised to aldehyde group. This reaction is called **Etard's reaction.**



Benzaldehyde

Thus,



Benzoic acid — Benzaldehyde

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Mechanism : Electrophilic substitution reactions of Benzene

The orbital structure of benzene makes it quite clear that the π-electron cloud lying above and below the plane of the benzene ring is held loosely and is thus, available to the electron seeking reagents *i.e.*, electrophiles. Therefore, the substitution reactions in benzene are electrophilic in nature. These reactions are characteristic not only of benzene ring itself but also of the compounds where benzene ring is present. The various electrophilic substitution reactions of benzene follow the same path. The electrophilic substitution reactions proceed via the following three steps :

1. *Generation of the electrophile*
2. *Formation of carbocation intermediate*
3. *Removal of proton from the carbocation intermediate to form the product.*

Step 1. Generation of the electrophile

The attacking reagent may not be a strong electrophile. Therefore, first of all an electrophile is generated by some preliminary reaction.

$$\underset{\text{Reagent}}{E\text{—}Nu} \longrightarrow \underset{\text{Electrophile}}{E^+} + \underset{\text{Nucleophile}}{:Nu^-}$$

For example, during chlorination of benzene, an electrophile (Cl^+) is generated by reacting with anhydrous $AlCl_3$ used as catalyst.

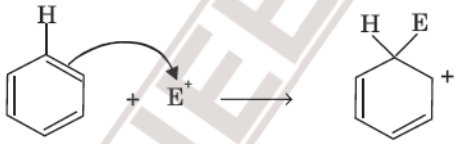
$$Cl_2 + AlCl_3 \longrightarrow \underset{\text{Chloronium ion}}{Cl^+} + AlCl_4^-$$

Similarly, during alkylation of benzene, electrolphile is generated as :

$$CH_3\text{—}Cl + AlCl_3 \longrightarrow \underset{\text{Electrophile}}{CH_3^+} + AlCl_4^-$$

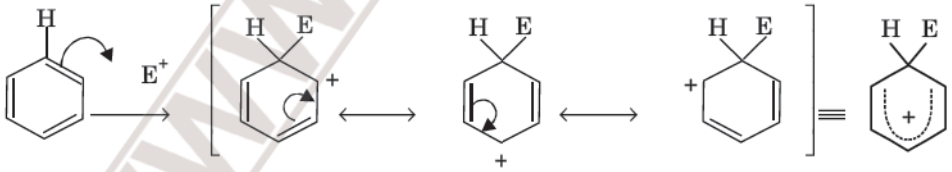
Step 2. Formation of carbocation, (arenium) intermediate.

The electrophile E^+ attacks the π–electron cloud of the aromatic ring and forms a bond with carbon, creating a positive charge on the ring. This results in the formation of a sigma complex or a carbocation (called arenium ion)



Sigma complex
(arenium ion)

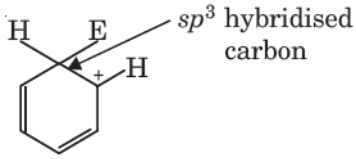
The arenium ion gets stabilized by resonance



Resonance stabilization of carbocation (arenium) intermediate.

The resulting carbocation has three important contributing structures which spread the positive charge over the remaining carbon atoms, although more on the carbon atoms that are *ortho* and *para* to the position attacked by the electrophile.

It may be noted that during the formation of sigma complex (arenium ion), the aromatic character of benzene ring is lost. This is because in the carbocation, one of the carbon is sp^3 hybridised and delocalisation of electrons stops at sp^3 hybridised carbon. Therefore this step is slow and hence is the **rate determining step** of the reaction.



Step 3. Removal of proton

The carbocation formed loses a proton to the nucleophile (Nu^-) present in the reaction mixture to form a substitution product. During this step, the aromatic character of the benzene ring is restored and this step is fast.

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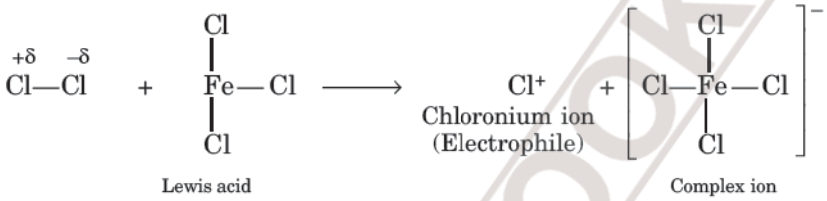
The loss of proton allows the two electrons from the carbon–hydrogen bond to move to regenerate the aromatic ring and thus restoring the aromatic character.

Thus, the electrophilic substitution in benzene involves *addition* followed by *elimination* and results in the desired substituted product.

Role of Catalysts in Electrophilic Aromatic Substitution

In almost all the electrophilic aromatic substitution reactions of benzene, a catalyst is generally required to generate a powerful *electrophile i.e.* the attacking reagent. The catalysts are usually *Lewis acids or protonic acids.* For example, chlorination of benzene requires the presence of a Lewis acid catalyst, usually ferric chloride. Ferric chloride being electron deficient in nature takes up a Cl^- ion from chlorine molecule to make it, polar ($Cl^{\delta+} - Cl^{\delta-}$) and to generate a highly reactive electrophile *i.e., chloronium ion* (Cl^+) as follows :



In the alkylation and acylation reactions of benzene, the catalyst employed is anhydrous aluminium chloride which is also a Lewis acid . Similarly, sulphuric acid acts as a catalyst in the nitration and sulphonation.

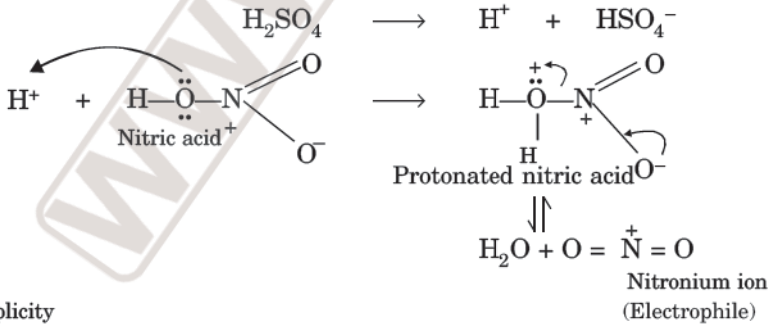
It is interesting to note that no catalyst is required in the electrophilic addition reactions of alkenes. In fact, there is no delocalisation of the π-electron charge in alkenes. The π-electron cloud can easily cause the polarisation of the attacking molecule to generate the electrophile. However, in benzene and other aromatic compounds, there is delocalisation of electron charge . The electron clouds are incapable of causing any polarisation of the attacking reagent. Hence, a catalyst *i.e.*, a Lewis acid or protonic acid is always required to generate the electrophile.

The mechanism of some important mono-substitution reactions of benzene are discussed below :

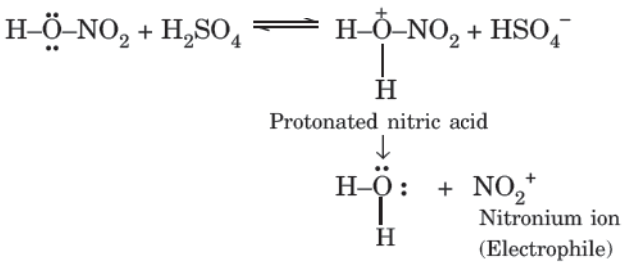
(1) Mechanism of Nitration of Benzene

In the nitration of benzene, a hydrogen atom of benzene is substituted by a nitro (NO_2) group. The attacking reagent is the *nitronium ion* (NO_2^+), whose formation is facilitated by the presence of sulphuric acid (catalyst). The mechanism is illustrated by the following steps :

1. The electrophile nitronium ion is generated as follows :



or for simplicity



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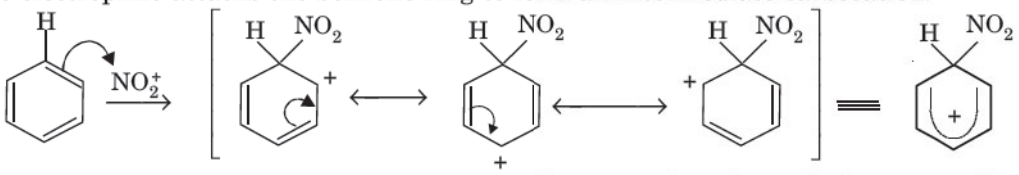
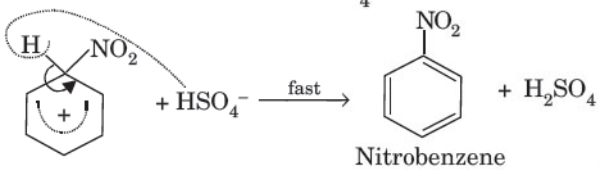
2. The electrophile attacks the benzene ring to form an intermediate carbocation.



3. The intermediate carbocation ion loses a H^+ to HSO_4^- ion and results in the formation of a nitro compound.



Nitrobenzene

(2) Mechanism of Sulphonation of Benzene

In the sulphonation of benzene, a hydrogen atom attached to the carbon atom of the ring gets substituted by a sulphonic acid group ($-SO_3H$). The attacking reagent is sulphur trioxide, SO_3 (neutral electron deficient species). It can be formed by the dissociation of sulphuric acid.

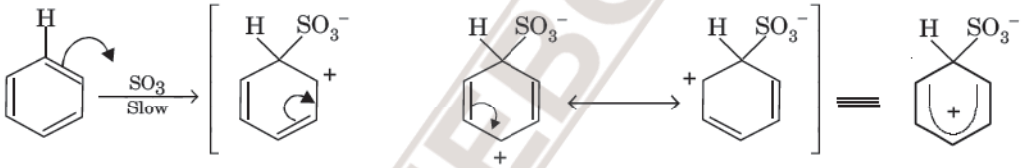
The sulphonation of benzene follows the following steps :

1. The electrophile SO_3 is generated as follows :

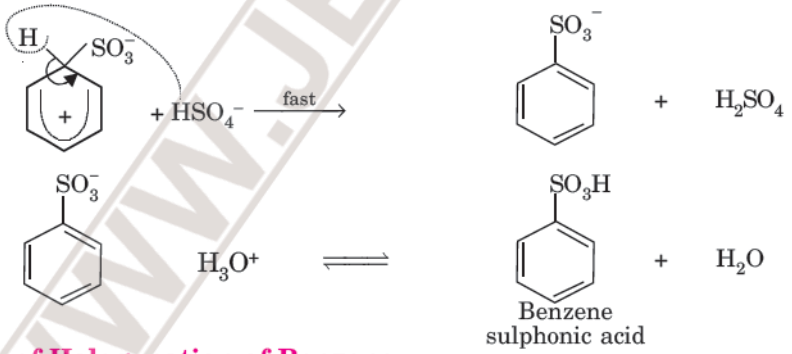
$$2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + \underset{\text{Electrophile}}{SO_3}$$

Sulphur atom in sulphur trioxide has only sextet of electrons. Therefore, the molecule is electron deficient in nature and acts as an electrophile.

2. The electrophile attacks the benzene ring to form an intermediate carbocation.



3. The intermediate carbocation loses a H^+ to HSO_4^- ion to form benzene sulphonate ion. This can take up a proton from H_3O^+ ion to form benzene sulphonic acid.



Benzene sulphonic acid

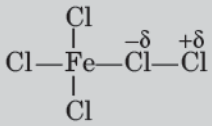
(3) Mechanism of Halogenation of Benzene

The chlorination or bromination of benzene is carried out by treating with chlorine or bromine in the presence of ferric salts *i.e.*, $FeCl_3$ or $FeBr_3$. The metal catalyst being a Lewis acid (Fe is electron deficient) polarises the halogen molecule and thus, generates an electrophile . The mechanism is being illustrated with the help of chlorination of benzene.

1. The electrophile (chloronium ion) is generated as follows :

$$\overset{+\delta\ \ \delta-}{Cl—Cl} + FeCl_3 \longrightarrow FeCl_4^- + \underset{\text{Chloronium ion}}{Cl^+}.$$

It has been suggested that free chloronium ion may not have actual existence. The electrophile is supposed to be made available from a complex between $FeCl_3$ and Cl_2.



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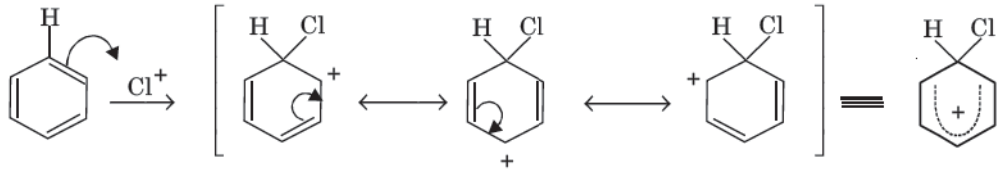
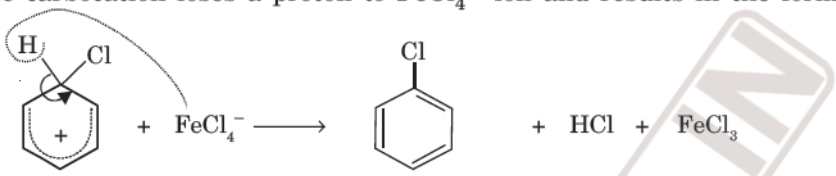
2. The electrophile attacks the benzene ring to form an intermediate carbocation.



3. The intermediate carbocation loses a proton to $FeCl_4^-$ ion and results in the formation of a chloro compound.



Chlorobenzene

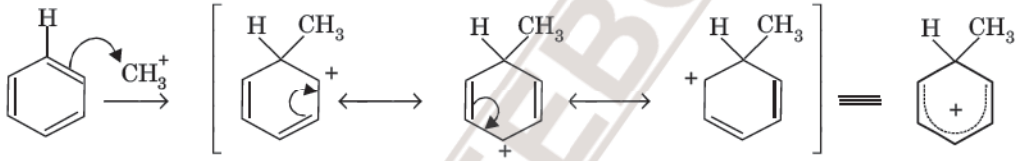
(4) Mechanism of Friedel–Craft Alkylation of Benzene

In the alkylation of benzene, one hydrogen atom attached to the carbon atom of the ring gets replaced by alkyl (–R) group. The attacking electrophile is an alkyl carbonium ion (R^+) made available by alkyl halide molecule. The release of electrophile is facilitated by the presence of anhydrous $AlCl_3$. The mechanism is being illustrated with the help of methyl chloride, CH_3Cl.

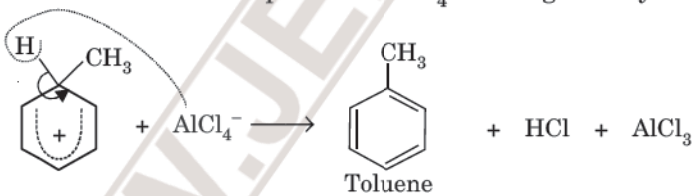
1. The electrophile (methyl carbocation) is generated as follows :

Methyl carbocation

2. The electrophile attacks the benzene ring to form an intermediate carbocation.

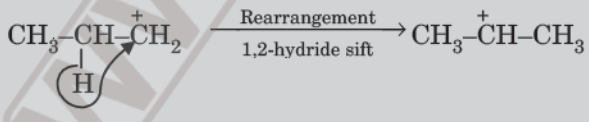


3. The intermediate carbocation loses a proton to $AlCl_4^-$ ion to give alkylated product.



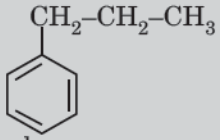
Toluene

Note. When the alkylation is carried with higher alkyl halides such as *n*-propyl chloride, the electrophile formed in the first step is a primary carbocation ($CH_3–CH_2–CH_2^+$). Being extremely unstable, it changes to a more stable secondary carbocation by the rearrangement reaction.

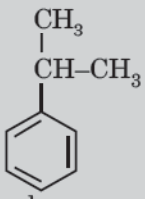


Primary carbocation (1°) Secondary carbocation (2°)

Thus, the electrophile is $(CH_3)_2CH^+$ ion and the product formed is 2-phenyl propane and not 1-phenyl propane.



1-Phenyl propane
(n-propyl benzene)
(not possible)



2-Phenyl propane
(isopropyl benzene)
(possible)

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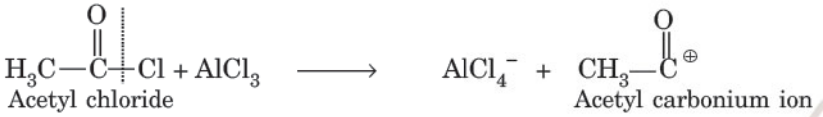
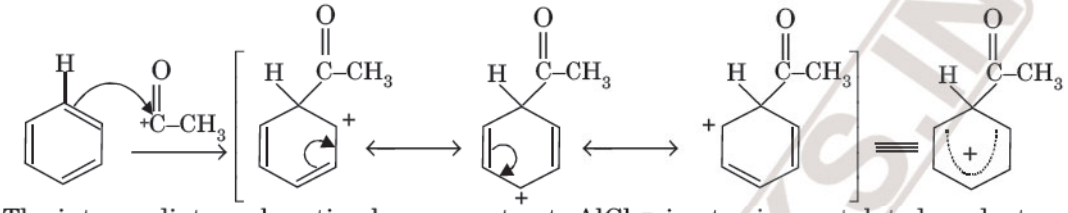
(5) Mechanism of Friedel Crafts Acylation

In acylation of benzene, the hydrogen attached to the carbon atom of the ring gets replaced by acyl (RCO–) group. The attacking electrophile ; an acyl carbocation ($R\overset{\oplus}{C}O$) is supplied by acid chloride (RCOCl) in the presence of anhydrous $AlCl_3$. The mechanism is illustrated with the help of acetyl chloride, CH_3COCl.

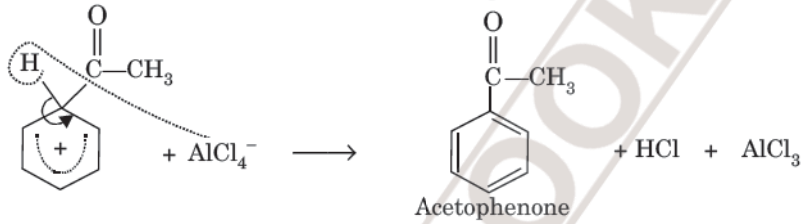
1. The electrophile (acetyl carbocation) is generated as follows :



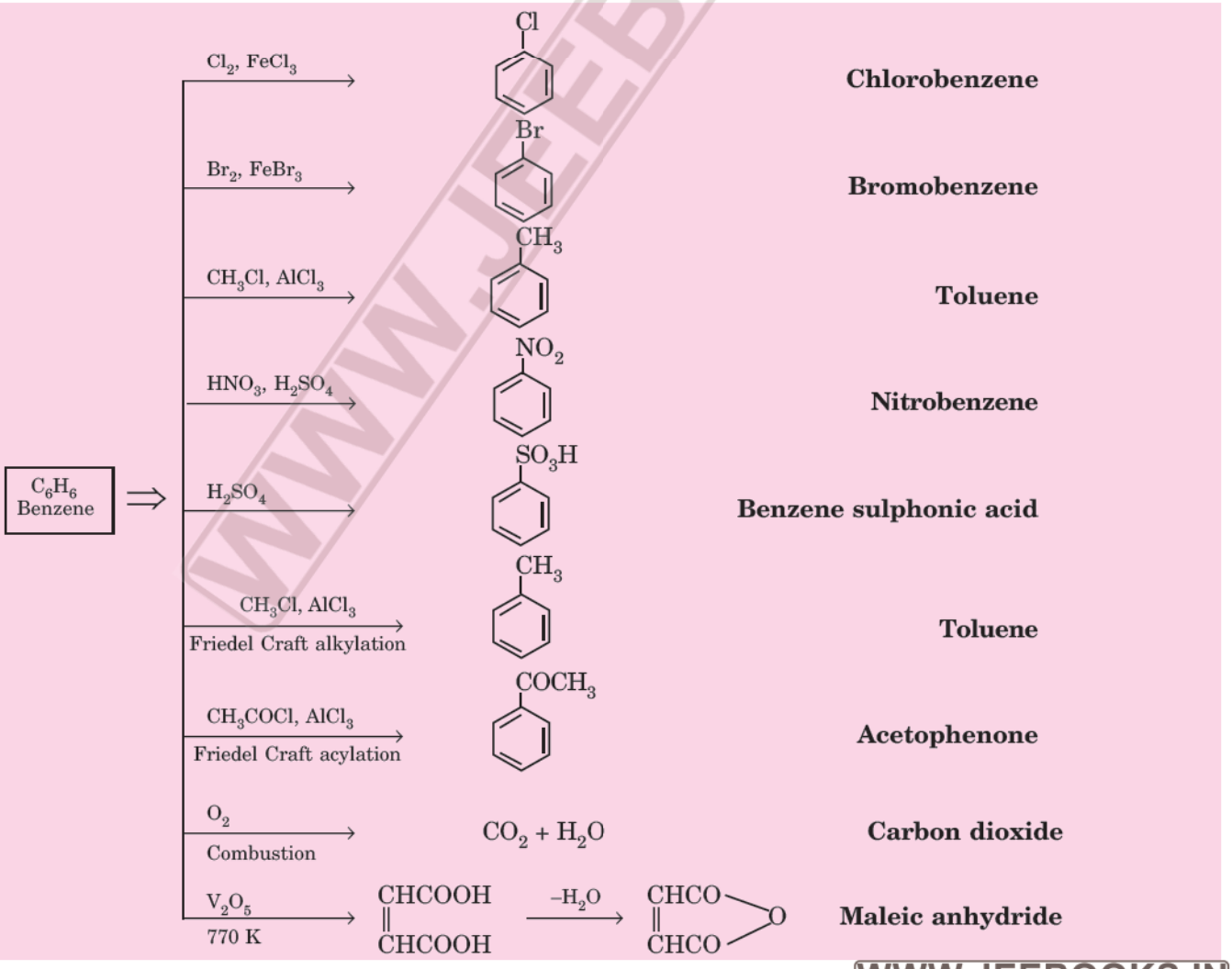
2. The electrophile attacks the benzene ring to form an intermediate carbocation.



3. The intermediate carbocation loses a proton to $AlCl_4^-$ ion to give acetylated product.



The reactions of benzene are **summed** up below.



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DIRECTIVE INFLUENCE OF SUBSTITUENTS AND THEIR EFFECT ON REACTIVITY

As we have learnt, all the six hydrogen atoms of benzene ring are equivalent. Therefore, replacement of any one of these six hydrogen atoms by any substitution always forms a single mono substituted product. However, when monosubstituted benzene is subjected to further substitution, the group present on the benzene ring affects the incoming attacking groups.

The ability of a group already present in the benzene ring to direct the incoming group to a particular position is called the directive influence of groups.

A substituent already present on the ring has two effects :

(*i*) **Orientation effect –** Substituents affect the orientation of the reaction. The three possible disubstituted products *i.e ortho*, *meta* and *para* are not formed in equal amounts. The nature of the substituent already present on the benzene ring determines the position of the second substitution. Some groups direct substitution primarily to the ortho and para positions, while other groups direct substitution primarily to the meta position. In this way, it has been found that every group can be put into one of the two classes : *ortho* and *para director* or *meta director.*

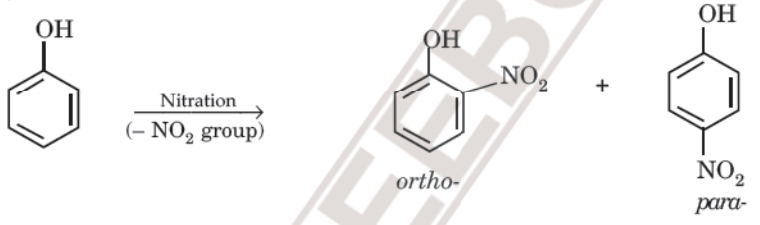
***(ii)* Reactivity –** The substituents affect the reactivity of the aromatic ring. Some substituents **activate** the ring and therefore make it more reactive than benzene. On the other hand, some groups **deactivate** the ring and make it less reactive than benzene. For example, in aromatic nitration, the –OH group makes the ring more reactive than benzene, whereas a $-NO_2$ substituent makes the ring less reactive.

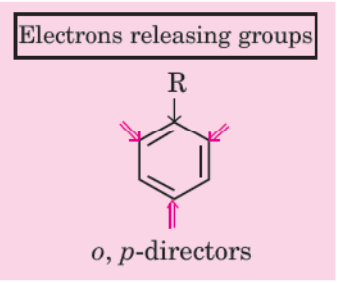
The substituents can be classified into three groups :

1. Ortho and para-directing activators. These groups release electrons and activate the benzene ring. These groups direct the incoming groups to *ortho* and *para* positions. The common examples are :

—OH, —OCH_3,—$OCOCH_3$, —NH_2,—$NCHCH_3$,—$NHCOCH_3$, —CH_3, etc.

For example,

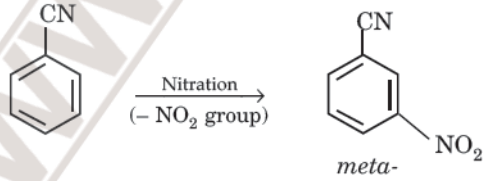


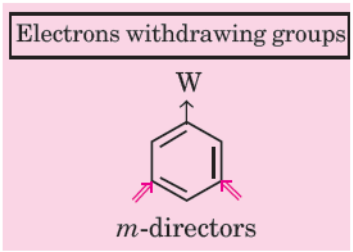


2. Meta directing deactivating groups. These groups withdraw electrons from the benzene ring and deactivate it. These groups direct the incoming group to **meta positions.** The common examples are :

–NO_2, –CN, –CHO, –COOH, –SO_3H, –$COCH_3$,.

For example,

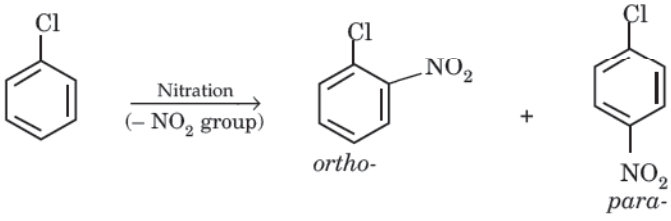


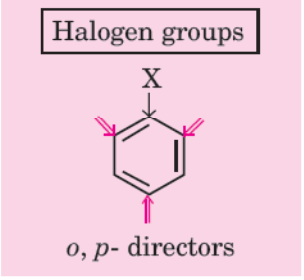


3. Ortho and para directing deactivating groups. These groups withdraw electrons from the benzene ring and deactivate it. However, these direct the incoming group to ortho and para positions. The common examples are :

Halogens : –F, Cl ,Br, I.

For example,





The halogens have unique character in being weakly deactivating but *ortho* and *para* directing. These groups are summed up in Table 2.

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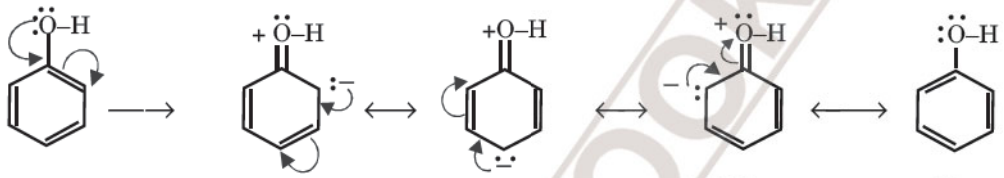
Table 2. Effect of groups on electrophilic substitution reactions.

Ortho and *para* directing activators	*Meta* directing deactivators	*Ortho* and *para* directing deactivators
$-NH_2$	$-NO_2$	– F
– OH	– CN	– Cl
– NHR, $-NR_2$	$-N(CH_3)_3^+$	– Br
$-OCH_3$, $-C_2H_5$	– COOH	– I
$-NHCOCH_3$	$-SO_3H$	
$-CH_3$	– CHO	
$-C_6H_5$	– COR	

There is no *meta* directing activator group.

Explanation for different directive influence

Ortho and para directing groups. As an example, let us discuss the directive influence of –OH (phenolic) group. The resonance structures of phenol are shown below :

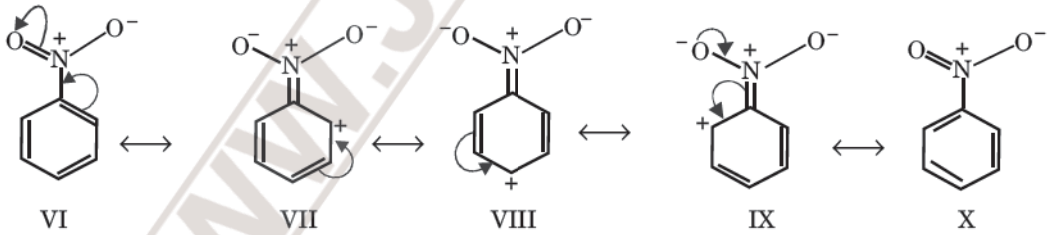


I II III IV V

Resonance structures of phenol.

The resonance structures of phenol show that the overall electron density on the benzene ring increases in comparison to benzene. Therefore, it is an **activating group.** The typical reactions of aromatic hydrocarbons are electrophilic substitution reactions in which an electrophile attacks the benzene ring. The structures II, III and IV show that the electron density is high at *ortho* and *para* positions and therefore, the electrophile will preferentially attack *ortho* and *para* positions. Thus, –OH group is ***o*- and *p*-directing group.** Similarly, other groups such as $-NH_2$, $-NR_2$, $-OCH_3$, $-CH_3$, etc. are *ortho* and *para* directing groups.

Meta directing groups. As an example, let us discuss the directive influence of nitro ($-NO_2$) group. The resonance structures of nitrobenzene are shown below :

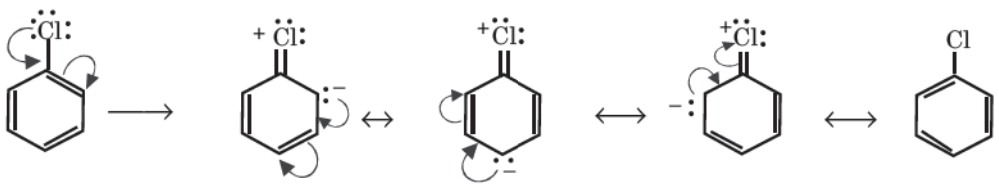


VI VII VIII IX X

Resonance structures of nitrobenzene

It is clear from the resonance structures that the overall electron density on the benzene ring decreases and therefore, this group is **deactivating group.** Moreover, the electron density on the *o*- and *p*-positions is less than on *m*-position. Therefore, the two *meta* positions are rich in electron density, thus resulting *m*-substitution. Other groups such as –COOH, $-SO_3H$, – CN, –CHO and –COR are meta directing groups.

Directive influence of halogens. The halogens are highly deactivating because of their strong negative inductive effect (–I effect). Therefore, the overall electron density on the benzene ring decreases. However, due to resonance the electron density on *o*- and *p*- positions is more as shown below and therefore, these are *o*- and *p*-directing. The resonance structures of chlorobenzene are shown below :



XI XII XIII XIV XV

Resonance structures of chlorobenzene

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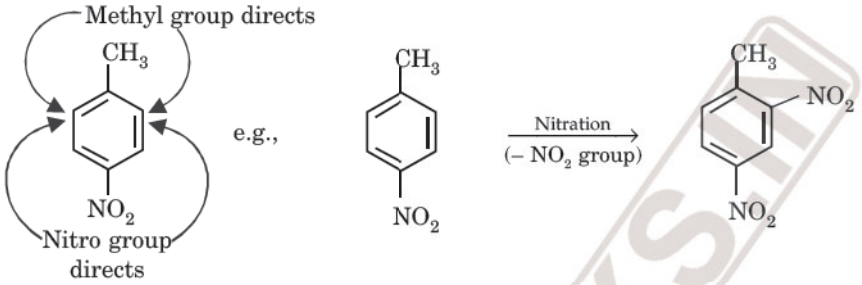
Reactivity and orientation in electrophilic substitution can be explained by the combined effects of **inductive effect** and **resonance effect.**

Orientation in Disubstituted Benzene

The presence of two substituents on the benzene ring makes the problem of orientation more difficult. This can be decided on the basis of three rules :

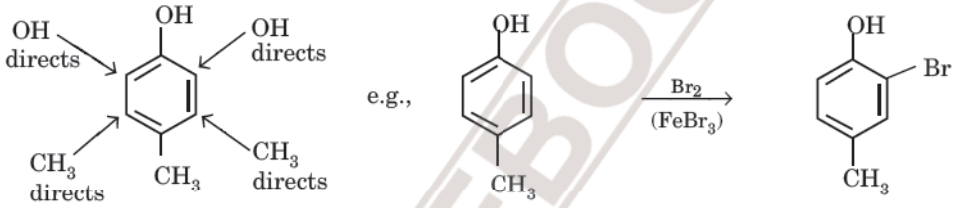
1. If the directing effects of two substituents reinforce, then a single product is formed. For example, in p-nitrotoluene, both the methyl and the nitro group direct further substitution to the same position (***ortho*** to methyl and ***meta*** to nitro)



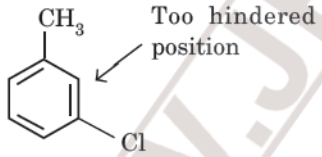
2. If the directing effect of the two groups oppose each other, strongly activating groups win over deactivating or weakly activating groups. The sequence of directing power is

$-NH_2 > -OH > -OCH_3 > -NHCOCH_3 > -C_6H_5 > -CH_3 >$ *meta* directors.

For example, during bromination of *p*–methyl phenol, –OH group is more powerful activator and therefore, controls the product.

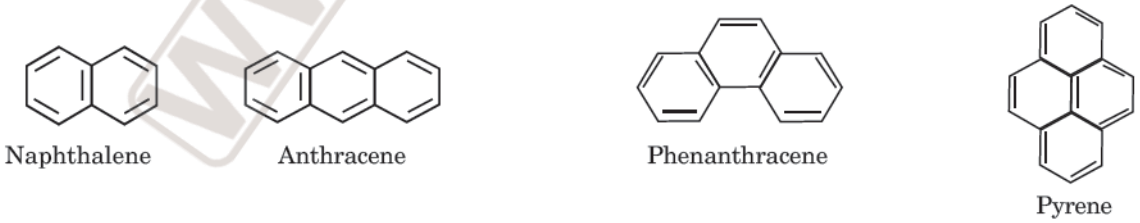


3. There is normally little substitution when the two groups are meta to each other. Aromatic rings with three adjacent substituents are generally prepared by some other routes.



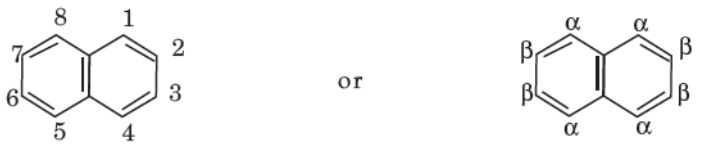
POLYNUCLEAR HYDROCARBONS

Polynuclear hydrocarbons contain two or more benzene rings fused together. These are also called **polycyclic aromatic compounds.** For example, naphthalene contains two benzene rings fused together. Other common examples are anthracene, phenanthracene, etc.



The major source of these polynuclear hydrocarbons is coal tar.

Positions in the naphthalene ring are indicated by numbers as :



Two isomeric monosubstituted naphthalenes are differentiated by prefixes 1- and 2- or α - and β-

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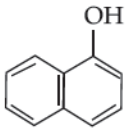
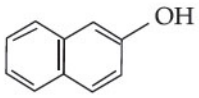


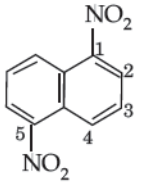
α-Naphthol
or 1-Naphthol

or



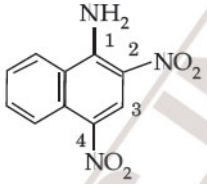
β-Naphthol
or 2-Naphthol

For highly substituted naphthalenes, the positions of the groups are indicated by numbers :



1, 5-Dinitronaphthalene

or



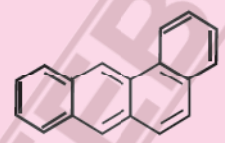
2, 4-Dinitro-1-naphthylamine

Naphthalene and other polynuclear aromatic hydrocarbons show many of the chemical properties similar to benzene.

The volatile arenes are highly inflammable and burn with a yellow sooty flame. Many of these polynuclear aromatic hydrocarbons are toxic and some are carcinogenic.

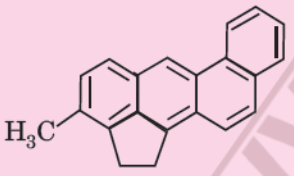
Carcinogenicity and Toxicity of Polynuclear Hydrocarbons

Most polynuclear hydrocarbons are carcinogenic in nature. It has been observed that the people who work under prolonged exposure to coal tar tend to suffer from skin cancer. A group of British chemists have studied that high boiling fluorescent fraction of coal tar produces cancer. The major component of this fraction was found to be 1, 2-benzanthracene.

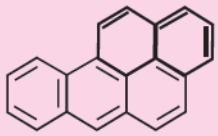


1, 2-Benzanthracene

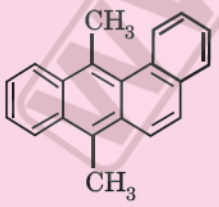
Later researches have shown that many other polynuclear hydrocarbons such as 3-methylcholanthracene, 1,2-benzpyrene, 9, 10-dimethyl-1,2-benzanthracene, etc. are carcinogenic in nature.



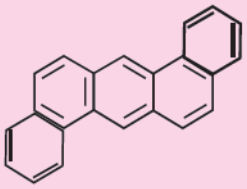
3-methylcholanthracene



1, 2-Benzpyrene



9, 10-Dimethyl-1, 2-benzanthracene



1, 2, 5, 6-Dibenzanthracene

It may be noted that there is no general rule by which one can predict the carcinogenic activity of hydrocarbons or their derivatives. However, the number and position of some groups such as $-CH_3$, –OH, –CN, $-OCH_3$, etc. have been found to influence the carcinogenic activity of polynuclear hydrocarbons.

Such polynuclear hydrocarbons are formed by incomplete combustion of organic materials such as coal, petroleum, tobacco, etc. When these polynuclear hydrocarbons enter into human body, they undergo various biochemical reactions and finally damage DNA and ultimately leads to cancer.

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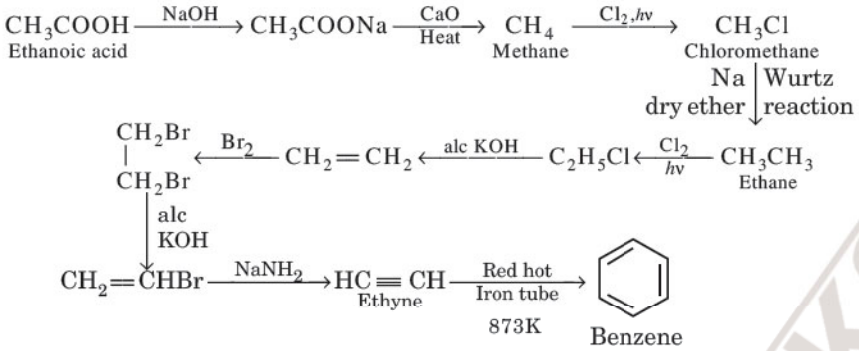
SOLVED EXAMPLES

Example 27.

How will you convert ethanoic acid into benzene ?. **N.C.E.R.T.**

Solution:

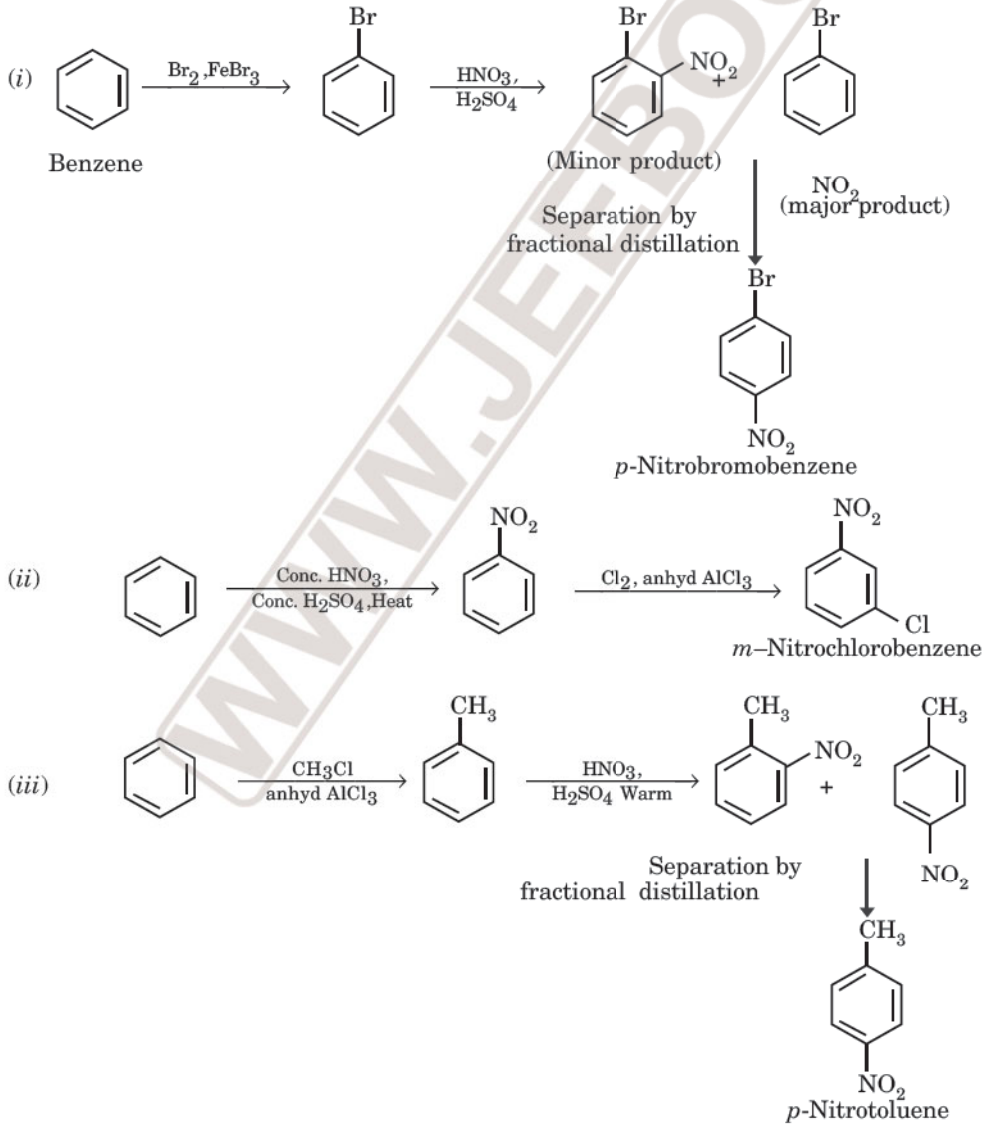


Example 28.

How will you convert benzene into

(i) p–nitrobromobenzene (ii) m–Nitrochlorobenzene (iii) p–nitrotoluene (iv) acetophenone

Solution: **N.C.E.R.T.**



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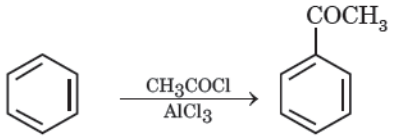
(*iv*) 

Acetophenone

Practice Problems

30. Complete the reaction :

$$C_6H_6 \xrightarrow{O_3} A \xrightarrow{Zn,\ H_2O} B$$

31. Complete the reaction :

$$B \xleftarrow{MnO_2,\ H^+} C_6H_5CH_3 \xrightarrow[Heat]{KMnO_4,\ H^+} A$$

32. What is difference between alkylation and acylation ?

33. What is halogen carrier ? Give one example.

34. What is Huckel rule ?

35. Which of the following are *meta* directors ?

$-NO_2$, $-SO_3H$, $-Cl$, $-OH$, $-NH_2$, $-CHO$

36. Name an *ortho*-and *para*-directing deactivating group.

Answers to Practice Problems

30. Benzene triozonide, glyoxal
31. A = C_6H_5COOH, B = C_6H_5CHO
33. $FeCl_3$ in halogenation of benzene
35. $-NO_2$, $-SO_3H$, $-CHO$
36. $-Cl$

Miscellaneous SOLVED EXAMPLES

Example 29.

Calculate the percentages of all the monochlorinated products obtained from 2-methylbutane. The relative reactivity of 1°, 2° and 3° hydrogen towards chlorination is 1 : 3.8 : 5.

(NCERT Exemplar Problem)

Solution: 2– Methylbutane is

$$\overset{1^\circ}{CH_3}-\overset{3^\circ}{\underset{\displaystyle CH_3}{\underset{|}{CH}}}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}$$

Since there are nine 1° H atoms (CH_3 groups) in the molecule, there are nine possibilities of compound A.

$$Cl-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3 \qquad (A)$$

There are two 2° H atoms (one CH_2) in the molecule and therefore, there are two possibilities of compound B.

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 \qquad (B)$$

There is only one 3° H atom (one CH hydrogen) and therefore, there is only one possibility of compound C.

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}-CH_2-CH_3 \qquad (C)$$

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Relative amounts of A, B and C = No. of H atoms in molecule × Relative reactivity

	A(1°)	B(2°)	C(3°)
Relative amounts	9 × 1 = 9	2 × 3.8 = 7.6	1 × 5 = 5

Total amount of monohalogenated compounds = 9 + 7.6 + 5 = 21.6

$$\text{Percentage of A} = \frac{9}{21.6} \times 100 = 41.7\%$$

$$\text{Percentage of B} = \frac{7.6}{21.6} \times 100 = 35.2\%$$

$$\text{Percentage of C} = \frac{5}{21.6} \times 100 = 23.1\ \%$$

Example 30.

How will you distinguish pent-1-ene from n-pentane ?

Solution: Pent-1-ene and *n*-pentane can be distinguished by the following tests :

1. **Reaction with Br_2 in CCl_4.** Pent-1-ene will decolourise the brown colour of the solution of Br_2 in CCl_4. But *n*-pentane will not decolourise the colour of bromine at room temperature.

$$\underset{\text{Pent-1-ene}}{CH_3CH_2CH_2CH=CH_2} + \underset{\text{Brown}}{Br_2} \xrightarrow{CCl_4} \underset{\text{Colourless}}{CH_3CH_2CH_2\underset{Br}{CH}-\underset{Br}{CH_2}}$$

$$\underset{n\text{-Pentane}}{CH_3CH_2CH_2CH_2CH_3} + \underset{\text{Brown}}{Br_2} \xrightarrow{CCl_4} \text{No reaction}$$

2. **Reaction with cold dilute $KMnO_4$ (Baeyer's test).** Pent-1-ene will react with Baeyer's reagent and its colour will be discharged. *n*-Pentane does not react.

$$\underset{\text{Pent-1-ene}}{CH_3CH_2CH_2CH=CH_2} \xrightarrow{\text{alk. } KMnO_4} \underset{\text{Colourless}}{CH_3CH_2CH_2\underset{OH}{CH}-\underset{OH}{CH_2}}$$

$$\underset{n\text{-Pentane}}{CH_3CH_2CH_2CH_2CH_3} \xrightarrow{\text{alk. } KMnO_4} \text{No reaction}$$

Example 31.

Complete the following reactions :

(i) Isopropyl bromide $\xrightarrow[Heat]{alc.\ KOH} A \xrightarrow[Peroxide]{HBr} B$

(ii) n-Propyl alcohol $\xrightarrow[443\ K]{Conc.\ H_2SO_4} A \xrightarrow[Heat]{O_2,\ Ag} B$

(iii) 1, 1, 2, 2-tetrachloroethane $\xrightarrow[Heat]{Zn,\ alcohol} A \xrightarrow[675\ K]{Iron\ tube} B$

(iv) Acetylene $\xrightarrow{NaNH_2} A \xrightarrow{CH_3CH_2Br} B$

(v) Propyne $\xrightarrow[Quinoline]{H_2,\ Pd,\ BaSO_4} A \xrightarrow[(ii)\ Zn,\ H_2O]{(i)\ O_3} B$

Solution:

(i) $\underset{\text{Isopropyl bromide}}{CH_3\underset{Br}{CH}CH_3} \xrightarrow[Heat]{alc.KOH} \underset{\text{Propene}}{\underset{(A)}{CH_3CH=CH_2}} \xrightarrow[peroxide]{HBr} \underset{\text{1-Bromopropane}}{\underset{(B)}{CH_3CH_2CH_2Br}}$

(ii) $\underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow[443\ K]{conc.H_2SO_4} \underset{\text{Propene}}{\underset{(A)}{CH_3CH=CH_2}} \xrightarrow[Heat]{O_2,\ Ag} \underset{\text{Propylene oxide}}{\underset{(B)}{CH_3CH-CH_2\ (O)}}$

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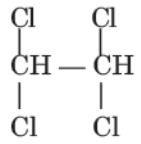
(*iii*)  $\xrightarrow[\text{Heat}]{\text{Zn, alcohol}}$ $HC \equiv CH$ (A) Ethyne $\xrightarrow[675\ K]{\text{Iron tube}}$ (B) Benzene

1, 1, 2, 2-tetrachloroethane

(*iv*) $HC \equiv CH \xrightarrow{NaNH_2} HC \equiv CNa \xrightarrow{CH_3CH_2Br} HC \equiv CCH_2CH_3$

Acetylene — (A) Sodium acetylide — (B) But-1-yne

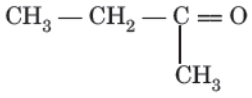
(*v*) $CH_3C \equiv CH \xrightarrow[BaSO_4]{H_2, Pd} CH_3CH = CH_2 \xrightarrow[(ii)\ Zn, H_2O]{(i)\ O_3} CH_3CHO + HCHO$

Propyne — (A) Propene — (B) Acetaldehyde + Formaldehyde

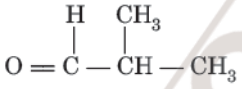
Example 32.

An alkene on ozonolysis gives butan-2-one and 2-methylpropanal. What products will be obtained when it is treated with hot conc. $KMnO_4$?

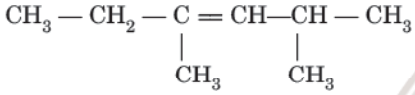
Solution: Let us first try to write the structure of alkene. The product of ozonolysis are :



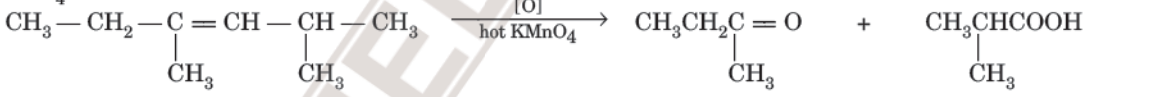
Butan-2-one



2-Methylpropanal

Alkene is 

With hot $KMnO_4$ it will react as :



Butan-2-one + 2-Methylpropanonic acid

Example 33.

An alkyl halide $C_5H_{11}Br$ (A) reacts with ethanolic KOH to give an alkene 'B', which reacts with Br_2 to give a compound 'C', which on dehydrobromination gives an alkyne 'D'. On treatment with sodium metal in liquid ammonia one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight chain alkane. Identify A, B, C and D. Give the reactions involved.

Solution: The reactions are : ***(NCERT Exemplar Problem)***

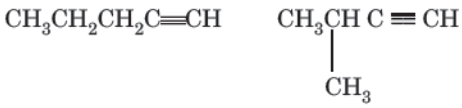
$C_5H_{11}Br \xrightarrow{\text{Alc.KOH}} C_5H_{10} \xrightarrow{Br_2} C_5H_{10}Br_2 \xrightarrow[\text{alc.KOH}]{\text{dehydrobromination}} C_5H_8$

Alkyl halide (A) — Alkene (B) — (C) — Alkyne (D)

$C_5H_8 \xrightarrow{Na,liq.NH_3} C_5H_7Na + \frac{1}{2}H_2$

(D) — Sodium alkylide

The reaction suggest that (D) is a terminal alkyne. The possible structures are :



(I) (II)

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Since alkyne (D) gives straight chain on complete hydrogenation, therefore, only structure (I) is possible. Hence the reactions may be written as :

$$CH_3CH_2CH_2CH_2CH_2Br \xrightarrow{\text{alc. KOH}} CH_3CH_2CH_2CH=CH_2 \xrightarrow{Br_2} CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2-Br$$

(A) (B) (C)

$$\xrightarrow{\text{alc. KOH}} CH_3CH_2CH_2C\equiv CH \xrightarrow{\text{Na, liq. } NH_3} CH_3CH_2CH_2C\equiv \bar{C}\ Na^+$$

(D)

and $$CH_3CH_2CH_2C\equiv CH \xrightarrow{2H_2} CH_3CH_2CH_2CH_2CH_3$$

Hence the structures of A, B, C and D are :

(A) $CH_3CH_2CH_2CH_2CH_2Br$

(B) $CH_3CH_2CH_2CH=CH_2$

(C) $CH_3CH_2CH_2CH(Br)CH_2Br$

(D) $CH_3CH_2CH_2C\equiv CH$

Example 34.

An unsaturated hydrocarbon 'A' adds two molecules of H_2 and on reductive ozonolysis gives butane-1, 4-dial, ethanal and propanone. Give the structure of 'A', write its IUPAC name and explain the reactions involved.

(NCERT Exemplar Problem)

Solution: Two molecules of hydrogen add on A and this means that 'A' is either an alkadiene or alkyne.

On reductive ozonolysis, 'A' gives three fragments and one of these is dialdehyde. Hence, the molecule has broken down at two sites. Therefore 'A' has two double bonds. The three fragments obtained on reductive ozonolysis are :

$OHC-CH_2-CH_2-CHO$, CH_3CHO, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=O$

Butane-1,4-dial Ethanal Propanone

The structure of 'A' as deduced from three fragments is

$$CH_3-\underset{\displaystyle H}{\underset{|}{C}}=O + O=\overset{\displaystyle H}{\overset{|}{C}}-CH_2-CH_2-\overset{\displaystyle H}{\overset{|}{C}}=O + O=C\begin{matrix}CH_3\\CH_3\end{matrix}$$

The hydrocarbon can be written by removing oxygen atoms and writing double bonds between the carbonyl carbon atoms :

$$\overset{8}{CH_3}-\overset{7}{CH}=\overset{6}{CH}-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-\overset{1}{CH_3}$$

IUPAC name : 2-Methylocta-2, 6-diene

Reactions are

$$CH_3-CH=CH-CH_2-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3 \xrightarrow{O_3} CH_3-\underset{\displaystyle O-O}{\overset{\displaystyle O}{\overset{/\ \backslash}{CH}}}-CH-CH_2-CH_2-\underset{\displaystyle O-O}{\overset{\displaystyle O}{\overset{/\ \backslash}{CH}}}-\overset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}$$

$$\xrightarrow{Zn,H_2O} CH_3-CHO + OHC\,CH_2\,CH_2\,CHO + O=C\begin{matrix}CH_3\\CH_3\end{matrix}$$

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❑ **Example 35.**

How will you convert :

(*a*) *Ethane to butane* (*b*) *Ethyne to methane*

(*c*) *Ethene to ethyne* (*d*) *Methane to ethane*

(*e*) *Propene to 2, 3-dimethylbutane* (*f*) *Ethane to ethyne*

(*g*) *Ethyne to but-2-yne*

Solution: (*a*) Ethane to butane :

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[\text{Sunlight}]{Cl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[\text{Wurtz reaction}]{2Na,\ \text{ether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

(*b*) Ethyne to methane

$$\underset{\text{Ethyne}}{HC\equiv CH} \xrightarrow[HgSO_4]{H^+,\ H_2O} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[K_2Cr_2O_7,\ H^+]{[O]} CH_3COOH \xrightarrow{NaOH} CH_3COONa \xrightarrow{NaOH,\ CaO} \underset{\text{Methane}}{CH_4}$$

(*c*) Ethene to ethyne

$$\underset{\text{Ethene}}{H_2C=CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\displaystyle Br\quad Br}{CH_2{-}CH_2} \xrightarrow{2\text{ alc. KOH}} \underset{\text{Ethyne}}{CH\equiv CH}$$

(*d*) Methane to ethane

$$\underset{\text{Methane}}{CH_4} \xrightarrow[\text{Sunlight}]{Cl_2} CH_3Cl \xrightarrow[\text{Wurtz reaction}]{Na,\ \text{ether}} \underset{\text{Ethane}}{CH_3CH_3}$$

(*e*) Propene to 2, 3-dimethylbutane

$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow{HBr} \underset{\displaystyle Br}{CH_3CHCH_3} \xrightarrow[\text{Wurtz reaction}]{Na,\ \text{ether}} \underset{\displaystyle CH_3\quad CH_3}{CH_3CH-CH-CH_3}$$

2, 3-Dimethylbutane

(*f*) Ethane to ethyne

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[\text{Sunlight}]{Cl_2} CH_3CH_2Cl \xrightarrow{\text{alc. KOH}} CH_2=CH_2 \xrightarrow{Br_2} \underset{\displaystyle Br\quad Br}{CH_2{-}CH_2} \xrightarrow{2\text{ KOH alc.}} \underset{\text{Ethyne}}{HC\equiv CH}$$

(*g*) Ethyne to but-2-yne

$$\underset{\text{Ethyne}}{HC\equiv CH} \xrightarrow{2NaNH_2} \underset{\text{Disodium acetylide}}{NaC\equiv CNa} \xrightarrow{2CH_3Br} \underset{\text{But-2-yne}}{CH_3C\equiv CCH_3}$$

❑ **Example 36.**

A hydrocarbon containing two double bonds gave on reductive ozonolysis ethanal, glyoxal and propanone. Predict the structure of the hydrocarbon and give its IUPAC name.

Solution: The products of reductive ozonolysis are (write the structures with their carbonyl groups facing one another).

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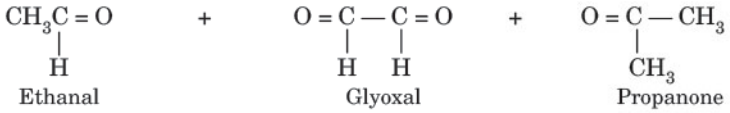
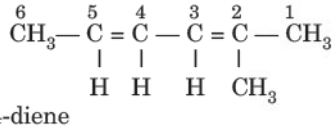


The hydrocarbon can be written by removing oxygen atoms and writing double bonds between the carbonyl carbon atoms :



IUPAC name : 2-Methylhexa-2,4-diene

Example 37.

Assign structures for the following :

(a) An alkyne (X) has molecular formula C_5H_8. It reacts neither with sodamide nor with ammoniacal cuprous chloride.

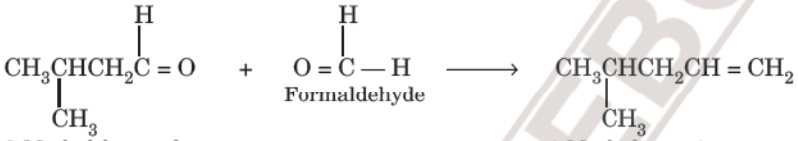
(b) A hydrocarbon 'Y' decolourises bromine water. On ozonolysis it gives 3-methyl butanal and formaldehyde. Give the name of the compound.

(c) A hydrocarbon (Z) has molecular formula C_8H_{10}. It does not decolourise bromine water and is oxidised to benzoic acid on heating with $K_2Cr_2O_7$. It can also have three other isomers A, B and C. Write the structures of Z, A, B and C.

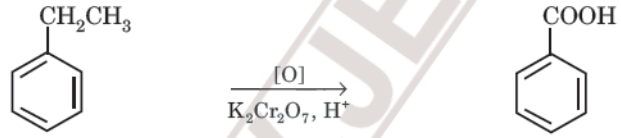
Solution: (*a*) Alkyne X is C_5H_8. Since it does not react with sodamide or ammoniacal cuprous chloride, the triple bond cannot be terminal.

$\therefore$ $X = CH_3CH_2C \equiv CCH_3$ Pent-2-yne

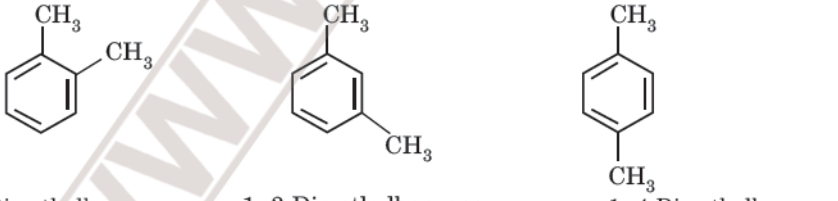
(*b*) Hydrocarbon 'Y' is alkene because it decolourises bromine water. From the products of ozonolysis, the structure of alkene can be predicted.



(*c*) Since it does not decolourise bromine water, it is arene. Its formula is



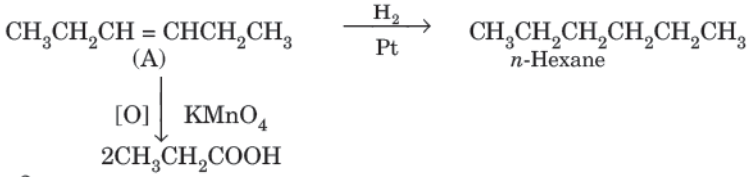
The other three isomers are :



Example 38.

The hydrocarbon A adds one mole of hydrogen in the presence of a platinum catalyst to form n-hexane. When A is oxidized vigorously with $KMnO_4$, a single carboxylic acid containing three carbon atoms is isolated. Give the structure of A and explain.

Solution:



$\therefore$ A is Hex-3-ene.

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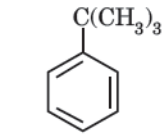
Example 39.

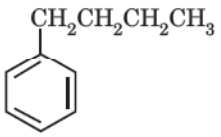
A monosubstituted alkyl benzene of the formula $C_{10}H_{14}$ resists vigorous oxidation to an aryl carboxylic acid. Name the compound and write its various monosubstituted isomers.

Solution: An alkyl group on benzene nucleus undergoes oxidation if it has at least one benzylic hydrogen atom. Since it resists oxidation, it means that it has no hydrogen on benzylic carbon. Therefore, it should be tertiary. So, the compound is **tert-butyl benzene** as

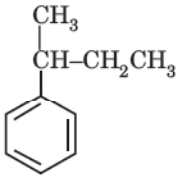


tert-butylbenzene

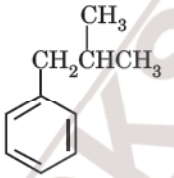
Other monosubstituted isomers are :



n-Butyl benzene



sec-Butyl benzene

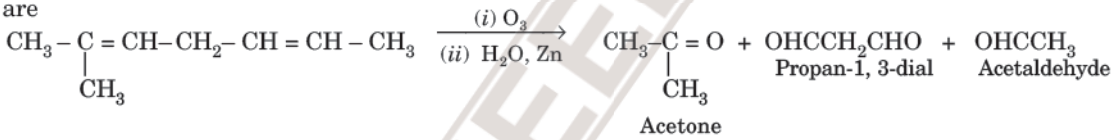


2-Methyl propyl benzene

Example 40.

A hydrocarbon 'X' takes up two molecules of hydrogen and is converted into a saturated hydrocarbon. On ozonolysis, X gives a mixture of three carbonyl compounds namely, acetaldehyde, acetone and propan-1, 3-dial. Assign structure to compound X.

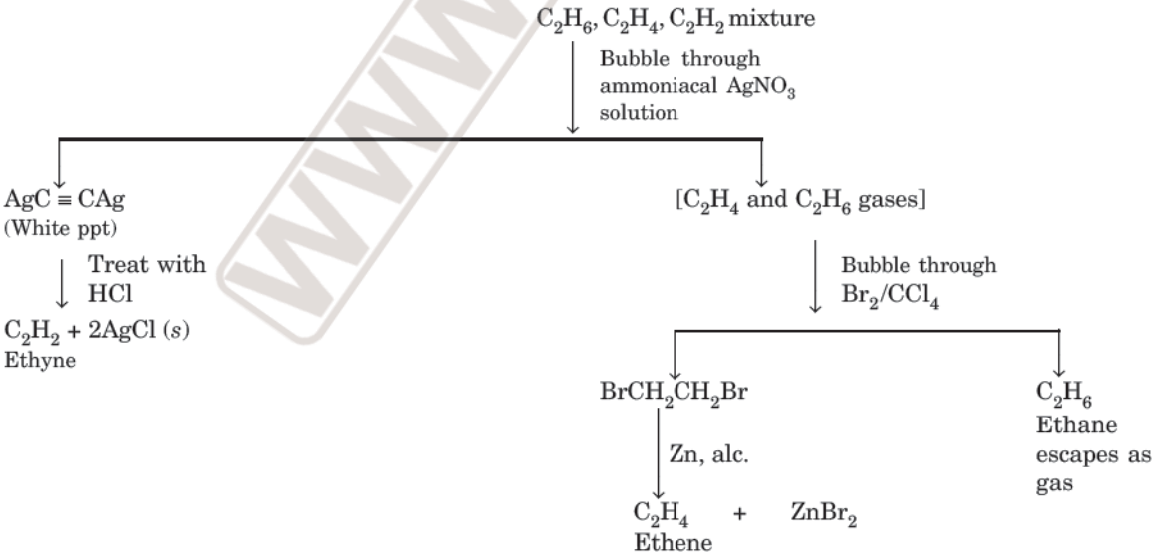
Solution: Since the compound takes up two molecules of hydrogen, it must have either a triple bond or two double bonds. The formation of three products on ozonolysis indicates that the compound has unsaturation at two places. The equations are



Example 41.

Suggest a method (a flow sheet) to separate a mixture of ethane, ethene and ethyne.

Solution: The flow sheet for separation of ethane (C_2H_6), ethene (C_2H_4) and ethyne (C_2H_2) is as follows :



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Example 42.

Write chemical equation for combustion reaction of the following hydrocarbons :
(i) Butane (ii) Pentene (iii) Hexyne (iv) Toluene **N.C.E.R.T.**

Solution:

(*i*) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g)$
Butane

(*ii*) $C_5H_{10}(g) + \frac{15}{2}O_2(g) \longrightarrow 5CO_2(g) + 5H_2O(g)$
Pentene

(*iii*) $C_6H_{10}(g) + \frac{17}{2}O_2(g) \longrightarrow 6CO_2(g) + 5H_2O(g)$
Hexyne

(*iv*) $C_7H_8(g) + 9O_2(g) \longrightarrow 7CO_2(g) + 4H_2O(g)$
Toluene

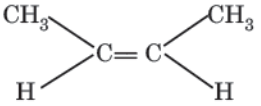
Example 43.

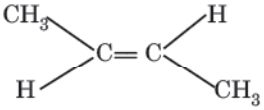
For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bonds as indicated : **N.C.E.R.T.**

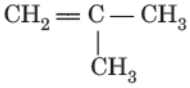
(i) C_4H_8 (one double bond) (ii) C_5H_8 (one triple bond)

Solution: (*a*)

(a) (*i*) $CH_2 = CH - CH_2 - CH_3$ But-1-ene

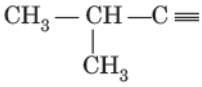
(*ii*)  *cis*-But-2-ene

(*iii*)  *trans*-But-2-ene

(*iv*)  2-Methylpropene

(*b*) (*i*) $HC \equiv C - CH_2 - CH_2 - CH_3$ Pent-1-yne

(*ii*) $CH_3 - C \equiv CH - CH_2 - CH_3$ Pent-2-yne

(*iii*)  3-Methylbut-1-yne

Example 44.

896 mL of a hydrocarbon 'A' having carbon 87.80% and hydrogen 12.19% weighs 3.28 g at STP. Hydrogenation of 'A' gives 2-methylpentane. Also 'A' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone 'B' having molecular formula $C_6H_{12}O$. The ketone 'B' gives a positive iodoform test. Find the structure of 'A' and give the reactions involved.

(NCERT Exemplar Problem)

Solution:

896 mL of C_xH_y (A) weigh = 3.28 g

22400 mL of C_xH_y (A) weigh = $\frac{3.28}{896} \times 22400$

= 82 g mol^{-1}

$\therefore$ Molecular mass of $C_x H_y$ = 82 g mol^{-1}

Determination of empirical formula

Element	%	Atomic mass	Relative ratio	Relative no. of atoms	Simplest ratio
C	87.8	12	87.80/12 = 7.31	7.31/7.31 = 1	3
H	12.19	1	12.19/1 = 12.19	12.19/7.31 = 1.66	4.98 $\simeq$ 5

Empirical formula of A = C_3H_5
Empirical formula mass = $3 \times 12 + 5 \times 1 = 41$

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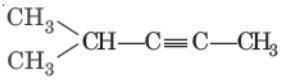
$$n = \frac{\text{Molecular formula mass}}{\text{Empirical formula mass}} = \frac{82}{41} = 2$$

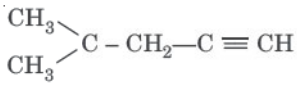
$\therefore$ Molecular formula = $(C_3H_6)_2 = C_6H_{10}$

Now C_6H_{10} (A) $\xrightarrow{2\text{ mole}}$ 2–Methylpentane $CH_3—\underset{\underset{Cl}{|}}{CH}—CH_2CH_2—CH_3$

The molecule has a chain of 5 carbon atoms with a methyl group at the second carbon atom. Since A adds a molecule of H_2O in the presence of Hg^{2+} and H^+ to give a ketone (B), it should be an alkyne. Two possible structures of 'A' are

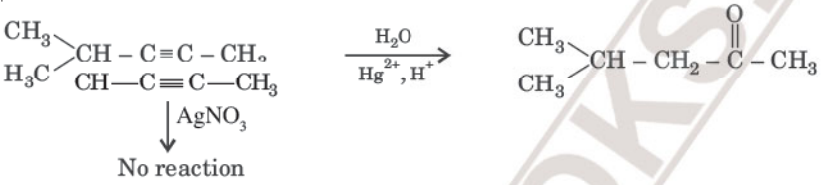


(I)



(II)

Since the compound B does not react with $AgNO_3$ solution, the triple bond is not terminal and therefore, structure (I) is the correct structure.



add on Conceptual Questions

Q.1. Why do alkynes not show geometrical isomerism ?

Ans. Alkynes have linear shape and therefore, do not show geometrical isomerism.

Q.2. Is it possible to isolate pure staggered ethane or pure eclipsed ethane at room temperature?

Ans. The energy difference between staggered and eclipsed forms of ethane is only 12.5 kJ mol^{-1}. This energy difference is very small and can be easily overcome by the collisions of the molecules at room temperature. Therefore, it is not possible to isolate either pure eclipsed or pure staggered form at room temperature.

Q.3. What is the difference between isomers and conformers ?

Ans. Isomers cannot be changed into one another and therefore, these are not interconvertible. On the other hand, conformers are interconvertible.

Q.4. What is the cause of geometrical isomerism in alkenes ?

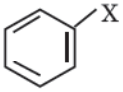
Ans. Alkenes have a π-bond and the restricted rotation around the π-bond gives rise to geometrical isomerism.

Q.5. Draw the two geometrical isomers of but-2-en-1, 4-dioic acid. Which of these will have higher dipole moment ?

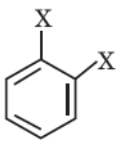
Ans.

Cis isomers will have higher dipole moment.

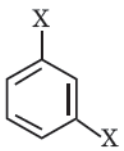
Q.6. How many isomers are possible for monosubstituted and disubstituted benzene ?

Ans. There is one monosubstituted benzene as 

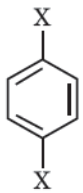
There are three disubstituted benzenes :



ortho



meta



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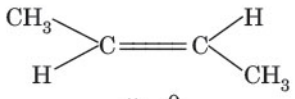
CONCEPTUAL QA

Q.7. Which of the two :
***trans*-but-2-ene or *trans*-pent-2-ene is non polar ?**

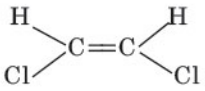
Ans. In *trans*-but-2-ene, the dipole moments of the two C—CH_3 bonds are equal and opposite and therefore, they cancel out each other. Hence, *trans*-2-butene is non-polar.



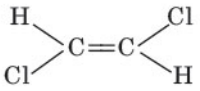
$\mu = 0$

Q.8. Write the structural formulae of all the possible isomers of $C_2H_2Cl_2$ and indicate which of these is non-polar ?

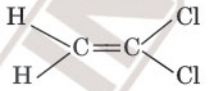
Ans.



(i) cis-1, 2-dichloroethene



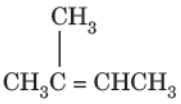
(ii) trans-1, 2-dichloroethene

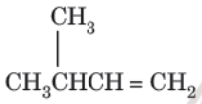


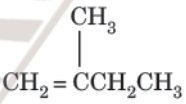
(iii) 1,1-dichloroethene

Out of these *(ii)* is non-polar.

Q. 9. Arrange the following alkenes in the decreasing order of stability :

(I) 

(II) 

(III) 

Ans. I > III > II

Q. 10. Why are 1, 4 adducts of 1, 3-butadiene are more stable than 1, 2-adduct ?

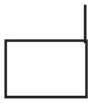
Ans. Because the alkene formed contains double bond which is more highly substituted.

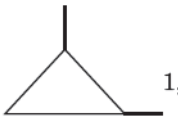
Q. 11. Which of the following is acidic :
But-2-ene, But-2-yne, But-1-yne, But-1-ene

Ans. But-1-yne

Q. 12. Draw the structures of three cycloalkane isomers with molecular formula C_5H_{10} each with a different size ring.

(i) Cyclopentane

(ii)  Methyl cyclobutane

(iii) 1, 1-Dimethyl cyclopropane or  1, 2-Dimethyl cyclopropane

Q.13. Arrange the following in increasing order of their release of energy on combustion :

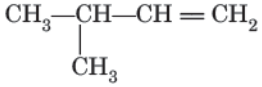
(i) ***(ii)*** ***(iii)*** ***(iv)***

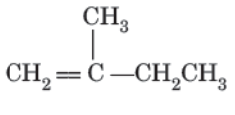
Ans. Largest the number of carbon atoms having maximum hydrogens (*i.e.*, CH_3 groups), greater is the heat of combustion. Thus, the increasing order of heat of combustion :
(iii) < *(iv)* < *(i)* < *(ii)*.

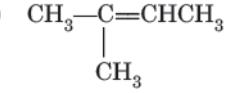
Q.14. Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+.
(*i*) chlorobenzene, 2, 4-dinitrochlorobenzene, *p*-nitrochloro benzene
(*ii*) toluene, *p*-$H_3C—C_6H_4—CH_3$, *p*—$H_3C—C_6H_4—NO_2$, *p*-$O_2N—C_6H_4—NO_2$

Ans. *(i)* Chloro benzene, *p*-nitrochloro benzene, 2, 4-dinitrochloro benzene.
(ii) *p*-$CH_3—C_6H_4—CH_3$ > toluene > *p*-$CH_3—C_6H_4—NO_2$, *p*-$NO_2—C_6H_4—NO_2$.

Q. 15. Write the structures of all alkenes which on hydrogenation give 2-methylbutane.

Ans. *(i)* 

(ii) 

(iii) 

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Q. 16. What effect the branching of an alkane has on its melting point ?

Ans. Branching of an alkane decreases the melting point.

Q. 17. Why is benzene extraordinarily stable though it contains three double bonds?

Ans. The extraordinarily stability of benzene is due to resonance. Due to resonance, the π-electron cloud gets delocalized resulting stability of molecule.

Q. 18. Suggest name of another Lewis acid instead of anhydrous aluminium chloride which can be used for ethylation of benzene.

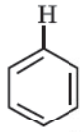
Ans. $FeCl_3$.

Q. 19. Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour.

Ans. Ethyne > benzene > *n*-hexane

This is because of maximum *s*-character in ethyne (50%) as compared to benzene (33%) and *n*-hexane (25%).

$HC \equiv CH$
Ethyne

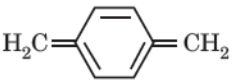

Benzene

$CH_3(CH_2)_4CH_3$
n-hexane

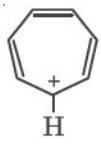
sp carbon (50% *s*-character) sp^2 carbon (33% *s*-character) sp^3 carbon (25% *s*-character)

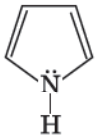
Q. 20. Which of the following compounds are aromatic according to Huckel rule?

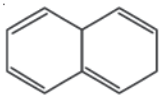
(*a*)

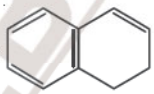
(*b*) 

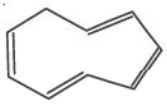
(*c*)

(*d*) 

(*e*) 

(*f*) 

(*g*) 

(*h*) 

Ans. (*d*), (*e*), (*g*) are aromatic. (g) is aromatic because out of 8π electrons, it has 6π delocalised electrons in one six membered planar ring, which obey Huckel rule and therefore, it is aromatic.

Q. 21. How will you prepare deuteriopropane ?

Ans. $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-I \xrightarrow{Mg.ether} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-MgI \xrightarrow{D_2O} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-D + Mg(OD)I$

Isopropyl iodide Deuteriopropane

Chapter Summary

Key Terms

- **Conformations** are the different arrangements in a molecule which can be obtained due to rotation around carbon-carbon single bond.
- **Staggered conformations** of ethane and propane are more stable than their eclipsed conformations.
- **Geometrical isomers:** The compounds which have same structural formula but differ in the spatial arrangement of atoms or groups of atoms around a double bond.
- **Markovnikov's rule.** During electrophilic addition across unsymmetrical double bond, the negative part of the adding molecule goes to that carbon atom which has lesser number of hydrogen atoms.

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QUICK CHAPTER ROUND UP

HYDROCARBONS

Saturated
contain C–C single bond
- alkanes

Unsaturated
contain carbon–carbon multiple bonds
- Alkenes (double bond)
- Alkynes (triple bond)

Aromatic
contain benzene ring
- Benzene, toluene

Alkanes: C_nH_{2n+2}

- Prepared by

$$RHC{=}CHR + H_2 \xrightarrow[\text{or Raney Ni}]{\text{Pd or Pt}} RCH_2\,CH_2R$$

- **Wurtz reaction**

$$CH_3I + 2Na + CH_3I \longrightarrow CH_3CH_3$$

Cannot be used for the preparation of alkanes with odd number of electrons.

- **Halogenation**

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

Reactivity of halogens

$F_2 > Cl_2 > Br_2 > I_2$

Rate of replacement of H of alkane

$3^\circ > 2^\circ > 1^\circ$

Mechanism

- Halogenation is a free radical substitution reaction.

$$(i)\ Cl_2 \xrightarrow{h\nu} Cl^\bullet + Cl^\bullet$$
$$(ii)\ Cl^\bullet + CH_4 \longrightarrow CH_3^\bullet + HCl$$
$$(iii)\ CH_3^\bullet + Cl_2 \longrightarrow CH_3Cl + Cl^\bullet$$

(*ii*), (*iii*) repeated till

$$Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$$
$$CH_3^\bullet + Cl^\bullet \longrightarrow CH_3Cl$$
$$CH_3^\bullet + CH_3^\bullet \longrightarrow CH_3CH_3$$

Alkynes: C_nH_{2n-2}

- Do not show geometrical isomerism
- **Alkynes are acidic**
  $HC \equiv CH > H_2C{=}CH_2 > CH_3{-}CH_3$
- **Acidity among alkynes**
  $HC \equiv CH > CH_3{-}C \equiv CH > CH_3{-}C \equiv C{-}CH_3$
- Terminal alkynes react with alkaline silver nitrate solution to give white ppt. This is test for distinguishing 1-Alkynes and 2-Alkynes.

$$CH_3C \equiv CH \xrightarrow[Zn, H_2O]{O_3} CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}H$$

2-Oxopropanal

$$3CH \equiv CH \xrightarrow[873\,K]{\text{red hot tube}} C_6H_6$$

$$\underset{\text{But-2-yne}}{CH_3C \equiv CCH_3} \underset{}{\overset{NaNH_2}{\rightleftharpoons}} \underset{\text{But-1-yne}}{CH_3CH_2\,C \equiv CH}$$

Alkenes: C_nH_{2n+2}

- Formed by dehydration of alcohols
- During dehydration of alcohols, the carbocation formed rearranges to stable carbocation.

e.g., $CH_3CH_2CH_2CH_2OH \xrightarrow{H^+} \underset{\text{But-2-ene (80\%)}}{CH_3CH{=}CHCH_3}$

- Reduction of alkynes
  with Lindlar's catalyst $\Longrightarrow$ cis-isomer
  with Birch reduction $\Longrightarrow$ trans-isomer
- Exhibit geometrical isomerism
- Similar atoms or groups on double bond
  same side $\Rightarrow$ cis
  opposite side $\Rightarrow$ trans
- For **geometrical isomerism**
  - the molecule must have a double bond and the two atoms or group of atoms attached to the same carbon atom must be different.
  - trans isomer is more stable than cis-isomer
- Greater the number of alkyl groups attached to the double bonded carbon atoms, the more stable is the alkene.

$R_2C{=}CR_2 > R_2C = CHR > RCH = CHR > R_2C{=}CH_2 > RCH = CH_2 > CH_2 = CH_2$

- Addition to unsymmetrical multiple bond follows **Markovnikov's rule.**

  Negative part of attacking reagent joins with C atom carrying lesser number of H-atoms.

- In the presence of peroxides, **anti-Markovnikov rule** is followed.

$$CH_3CH = CH_2 \xrightarrow{HBr} \underset{\underset{\text{2-Bromopropane}}{\underset{\text{Markovnikov rule}}{}}}{CH_3\underset{\underset{Br}{|}}{CH}CH_3} \qquad CH_3CH_2CH_2Br \xrightarrow{\text{Peroxides}} \underset{\underset{\text{Anti-Markovnikov rule}}{}}{\text{1-Bromopropane}}$$

- ♦ Markovnikov rule occurs through the formation of carbocation.
- ♦ Anti-Markovnikov rule follows free radical mechanism.
- Ozonolysis indicates the position of double bond.

$$\underset{R'}{\overset{R}{}}C{=}C\underset{R'''}{\overset{R''}{}} \xrightarrow[Zn, H_2O]{O_3} \underset{R'}{\overset{R}{}}C{=}O + O{=}C\underset{R'''}{\overset{R''}{}}$$

$$-C{=}C- + KMnO_4 \longrightarrow -\underset{OH}{\overset{OH}{C}}{-}\underset{OH}{\overset{OH}{C}}-$$

Pink colour of Baeyer's reagent gets decolourised

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Electrolysis reactions for the preparation of alkane, alkene and alkyne.

- *Electrolysis of aqueous solution of sodium or potassium salt of acetic acid gives ethane* **(alkane)**

$$\underset{\text{Potassium acetate}}{CH_3COOK + CH_3COOK} \xrightarrow[\text{Electrolysis}]{(aq)} \underset{\text{Ethane}}{CH_3-CH_3}$$

- *Electrolysis of aqueous solution of potassium salt of succinic acid gives ethylene* **(alkene)**

$$\underset{\text{Potassium succinate}}{CH_2COOK\text{-}CH_2COOK} \xrightarrow[\text{Electrolysis}]{(aq)} \underset{\text{Ethylene}}{CH_2=CH_2}$$

- *Electrolysis of aqueous solution of potassium salt of fumaric acid gives acetylene* **(alkyne)**

$$\underset{\text{Pot. fumarate}}{CHCOOK\text{-}CHCOOK} \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH}$$

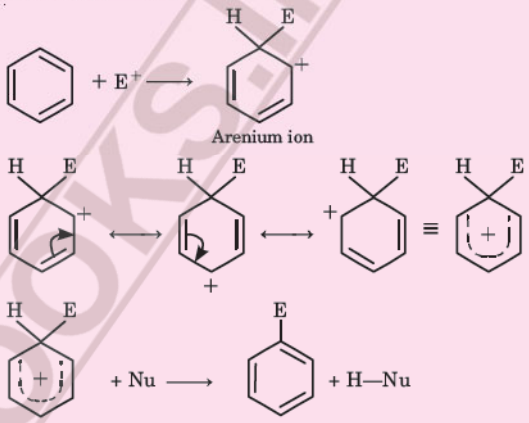
Aromatic Compounds

- Benzene is resonance hybrid of

- Aromaticity
  - planar
  - cyclic system
  - delocalized $(4n + 2)\ \pi$ electrons (Huckel Rule)

Benzene undergoes electrophilic substitution reactions.

$$Eu - Nu \longrightarrow E^+ + Nu$$

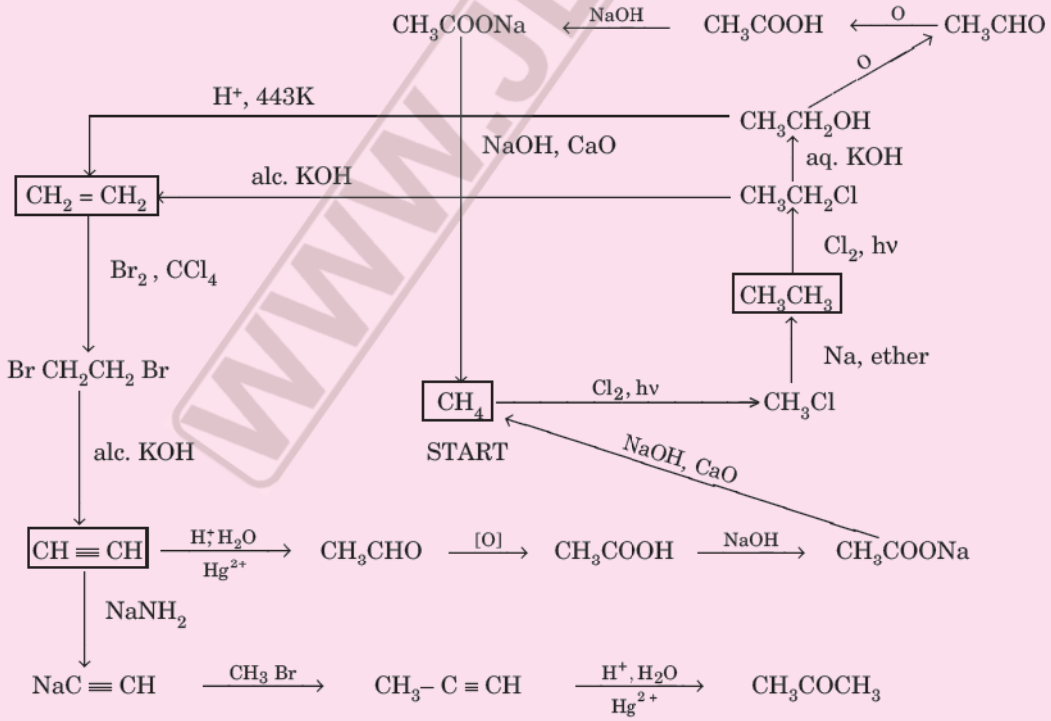


⇒ Ortho para directors (activators)
-OH, $-OCH_3$, $-OCOCH_3$, $-NH_2$, $-CH_3$
⇒ Meta directors (deactivators)
$-NO_2$, -CN, -CHO, -COOH, $-SO_3H$
⇒ Ortho para directors (deactivators)
halogens F, Cl, Br, I

Electrophiles in electrophilic substitution reactions

⇒ Nitration : NO_2^+
Sulphonation : SO_3
Acylation : RCO^+
Halogenation : X^+
Alkylation : R^+

CONVERSION ROUTES



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NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. How do you account for the formation of ethane during chlorination of methane ?

Ans. Chlorination of methane is a free radical reaction which occurs by the following mechanism :

(*i*) Chain initiation

$$Cl{-}Cl \xrightarrow[\text{Fission}]{\text{Homolytic}} \dot{Cl} + \dot{Cl}$$

(*ii*) Chain propagation

$$CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl{-}Cl \longrightarrow CH_3Cl + \dot{Cl}$$

(*iii*) Chain termination

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow \underset{\text{Ethane}}{CH_3 - CH_3}$$

$$\dot{C}H_3 + \dot{Cl} \longrightarrow CH_3Cl$$

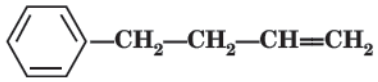
$$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$$

It is clear from the above mechanism, that the free radical $\dot{C}H_3$ may combine with itself to form ethane molecule.

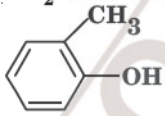
Q. 2. Write IUPAC names of the following compounds:

(*a*) $CH_3CH{=}C(CH_3)_2$ **(*b*)** $CH_2{=}CH{-}C{\equiv}C{-}CH_3$ **(*c*)**

(*d*)



(*e*)



(*f*) $CH_3(CH_2)_4CH(CH_2)_3CH_3$ with $CH_2{-}CH(CH_3)_2$

(*g*) $CH_3{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH(C_2H_5){-}CH_2{-}CH{=}CH_2$

Ans. (*a*) 2–Methylbut-2-ene

(*b*) Pent-1-en-3-yne

(*c*) Buta-1,3-diene

(*d*) 4-Phenylbut-1-ene

(*e*) 2-Methyl phenol

(*f*) 5–(2–Methylpropyl) decane

(*g*) 4-Ethyldeca-1,5,8-triene

Q. 3. For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated :

(*a*) C_4H_8 **(one double bond)** **(*b*)** C_5H_8 **(one triple bond)**

Ans. *Refer Solved Example 43. (Page 103).*

Q.4. Write IUPAC names of the products obtained by the ozonolysis of the following compounds :

(*i*) Pent-2-ene **(*ii*) 3,4-Dimethylhept-3-ene**

(*iii*) 2-Ethylbut-1-ene **(*iv*) 1-Phenylbut-1-ene**

Ans. (*i*) Pent-2-ene $\xrightarrow[(ii)\ Zn,\ H_2O]{(i)\ O_3,\ CH_2Cl_2}$ Propanal + Ethanal

(*ii*) 3,4–Dimethylhept-3-ene $\xrightarrow{\text{Ozonolysis}}$ Pentan-2-one + Butan-2-one

(*iii*) 2–Ethylbut-1-ene $\xrightarrow{\text{Ozonolysis}}$ Pentan-3-one + Methanal

(*iv*) 1-Phenylbut-1-ene $\xrightarrow{\text{Ozonolysis}}$ Propanal + Benzaldehyde

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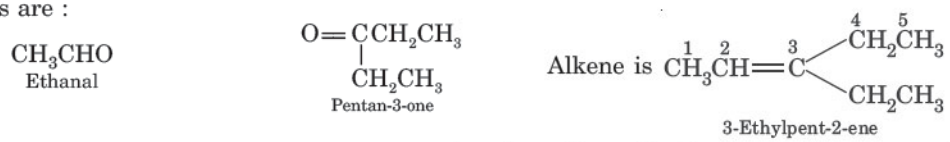
Q. 5. An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3- one. Write structure and IUPAC name of 'A'.

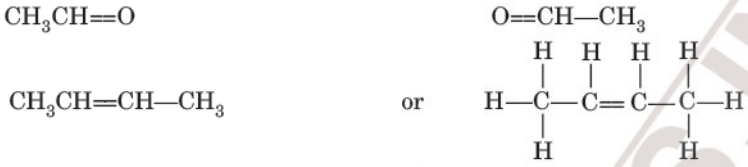
Ans. The products are :



Q. 6. An alkene 'A' contains three C—C, eight C—H σ-bonds and one C—C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44u. Write IUPAC name of 'A'.

Ans. An aldehyde having molecular mass of 44 a.m.u. is ethanal, CH_3CHO.

It gives two moles of ethanal



But-2-ene has three C—C, one C=C and eight C—H bonds.

Q. 7. Propanal and pentan-3-one are the ozonolysis products of an alkene ? What is the structural formula of the alkene ?

Ans. *Refer Solved Example 20 (Page 57).*

Q. 8. Write chemical equations for combustion reaction of the following hydrocarbons :

(*i*) Butane (*ii*) Pentane (*iii*) Hexyne (*iv*) Toluene

Ans. *Refer Solved Example 42 (Page 103).*

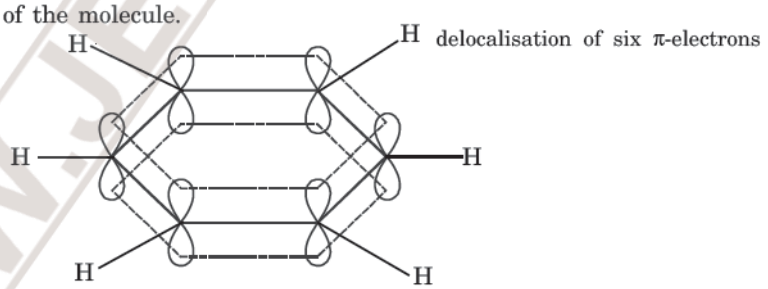
Q. 9. Draw the *cis* and *trans* structures of hex-2-ene. Which isomer will have higher b.p. and why ?

Ans. The structure of *cis*- and *trans*- hex-2-ene are :

cis-Hex-2-ene has large dipole moment and therefore will have stronger dipole-dipole interactions and hence higher boiling point.

Q. 10. Why is benzene extra ordinarily stable though it contains three double bonds ?

Ans. The extraordinary stability of benzene is due to resonance. In benzene, all the six π-electrons of three double bonds get delocalised resulting stability of the molecule.



Q. 11. What are the necessary conditions for any system to be aromatic ?

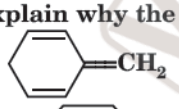
Ans. The necessary conditions for a molecule to be aromatic are :

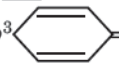
(*i*) The molecule should contain a cyclic cloud of delocalized π-electrons above and below the plane of the molecule.

(*ii*) For the delocalisation of π-electrons the ring must be planar to allow cyclic overlap of *p*-orbitals.

(*iii*) It should contain $(4n + 2)$ π-electrons where $n = 0, 1, 2, 3.....$. This is known as Huckel rule.

Q. 12. Explain why the following systems are not aromatic ?

(*i*)  **(*ii*)** **(*iii*)**

Ans. (*i*)  sp^3 contain one sp^3 hybridised carbon atom and therefore, the system is not planar. Though it contains 6π electrons but the system is not fully conjugated because all the six π-electrons donot form a cyclic electron cloud which surrounds all the atoms of the ring. Therefore, the compound is not aromatic.

(*ii*) is not aromatic because it contains one sp^3 hybridised carbon atom and the molecule is not planar.Moreover, it contains only 4π-electrons and does not obey Huckel rule *i.e.,* $(4n + 2)$ π-electrons.

(*iii*) is not aromatic because it is a non-planar system having 8π-electrons. Therefore, it does not obey Huckel rule *i.e.,* $(4n + 2)$π-electrons rule.

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Q. 13. How will you convert benzene into

(*i*) *p*-nitrobromobenzene (*ii*) *m*-nitrochlorobenzene (*iii*) *p*-nitrotoluene (*iv*) acetophenone ?

Ans. *Refer solved Example 28 (Page 95).*

Q. 14. In the alkane $H_3C—CH_2—C(CH_3)_2—CH_2—CH(CH_3)_2$, identify 1°, 2°, 3° carbon atoms and give the number of H-atoms bonded to each one of these.

Ans. *Refer Solved Example 6 (Page 27).*

Q. 15. What effect does branching of an alkane chain has on its boiling point ?

Ans. The boiling point of the alkanes decreases with branching. This is because with the increase in branching, the surface area of an alkane approaches that of a sphere. Since sphere has minimum surface are, therefore, van der Waals forces of attraction are minimum and hence boiling point decreases with branching.

Q. 16. Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

Ans. Addition of HBr to propene is an ionic electrophilic addition reaction which follows Markonikov rule. In this case, H^+ adds to alkene to give a more stable 2° carbocation. This is rapidly attacked by nucleophile Br^- ion to give 2-bromo propane.

$$H—Br \rightleftharpoons H^+ + Br^-$$

$$CH_3—CH=CH_2 + H^+ \xrightarrow{\text{Slow}} \underset{\text{2°-Carbocation (more stable)}}{CH_3—\overset{+}{C}H—CH_3}$$

$$CH_3—\overset{+}{C}H—CH_3 + Br^- \xrightarrow{\text{Fast}} \underset{\text{2–Bromopropane}}{CH_3—\underset{\displaystyle Br}{\underset{|}{C}}H—CH_3}$$

In the presence of benzoyl peroxide, the reaction follows free radical addition. In this case, $\dot{Br}$ free radical acts as electrophile which is obtained from the action of benzoyl peroxide on HBr.

$$C_6H_5CO—O—O—COC_6H_5 \xrightarrow[\text{Heat}]{\text{Homolytic fission}} 2C_6H_5CO\dot{O} \longrightarrow \underset{\text{Phenyl free radical}}{2C_6\dot{H}_5} + 2CO_2$$

$$C_6\dot{H}_5 + HBr \longrightarrow \underset{\text{Benzene}}{C_6H_6} + \dot{Br}$$

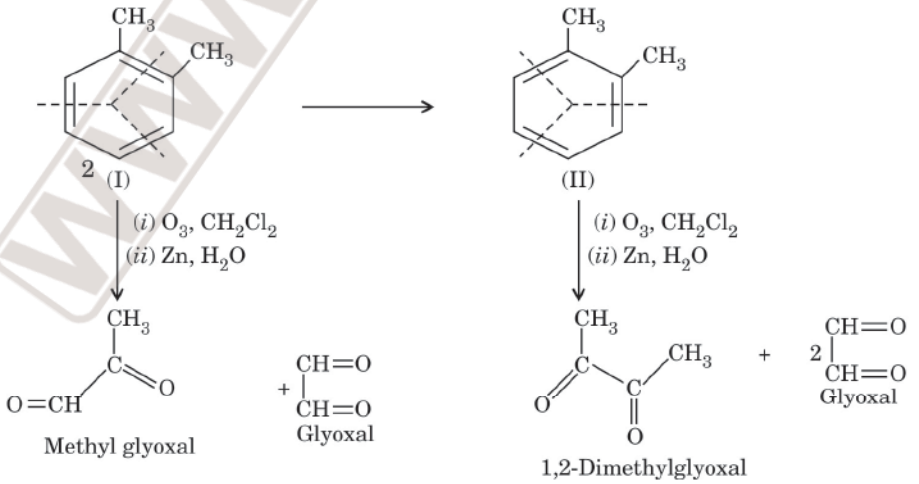
$\dot{Br}$ free radical attacks propene in such a way to generate a more stable 2° free radical. This free radical obtained rapidly abstracts a hydrogen atom of HBr to give 1-Bromopropane.

$$CH_3—CH=CH_2 + \dot{Br} \xrightarrow{\text{Slow}} \underset{\text{2°-Free radical (stable)}}{CH_3—\dot{C}H—CH_2Br}$$

$$CH_3—\dot{C}H—CH_2\,Br + H—Br \xrightarrow{\text{Fast}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} + \dot{Br}$$

Q. 17. Write down the products of ozonolysis of 1,2-dimethylbenzene (o-xylene). How does the results support the Kekule structure of benzene?

Ans. o-xylene may be regarded as a resonance hybrid of the following structures. Ozonolysis of each one of these gives two products as shown below:



Therefore, only three products are formed. Since all the three products cannot be obtained from any one of the two Kekule structures, this shows that o-xylene is a resonance hybrid of two Kekule structures (I) and (II)

Q. 18. Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

Ans. *Refer Conceptual Questions Q.19 (page 106).*

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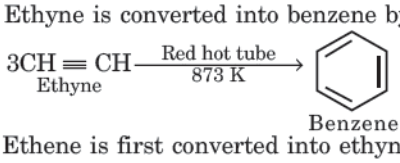
Q. 19. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty ?

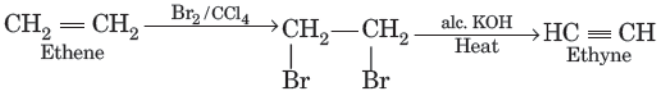
Ans. The orbital structure of benzene shows that the π-electrons cloud lying above and below the benzene ring is loosely held and is thus available to the π-electron seeking reagents *i.e.,* electrophiles. Therefore benzene undergoes electrophilic reactions readily and nucleophilic substitution reactions with difficulty.

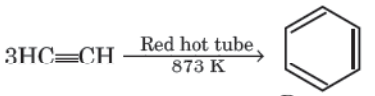
Q. 20. How would you convert the following compounds into benzene ?
(*i*) Ethyne (*ii*) Ethene (*iii*) Hexane

Ans. (*i*) Ethyne is converted into benzene by passing its vapours through red hot tube at 873 K.

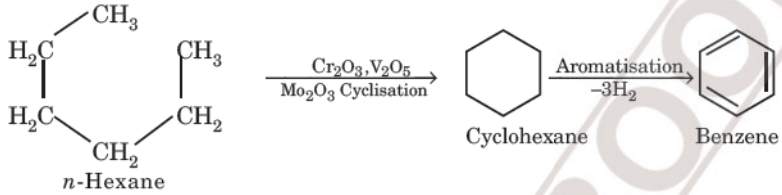


(*ii*) Ethene is first converted into ethyne and then to benzene as :



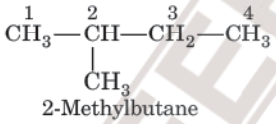


(*iii*) *n*-hexane is converted to benzene as :

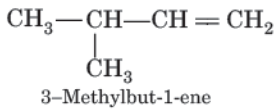


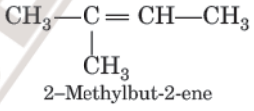
Q. 21. Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

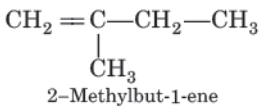
Ans. The product is



The different alkenes which give the product on hydrogenation are given below :







Q. 22. Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+. (a) Chlorobenzene, 2,4-dinitrochlorobenzene, *p*-nitrochlorobenzene.
(b) Toluene, *p*—H_3C—C_6H_4—NO_2, *p*—O_2N—C_6H_4—NO_2

Ans. *Refer Conceptual Questions, Q.14 (Page 105).*

Q. 23. Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why ?

Ans. CH_3 group is electron releasing group while —NO_2 group is electron withdrawing group. Therefore, the electron density will be more in toluene than in benzene and the electron density in *m*-dinitrobenzene will be less than in benzene. Therefore, the ease of nitration decreases in the order :

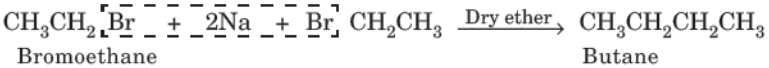
toluene > benzene > *m*-dinitrobenzene.

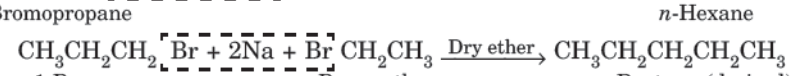
Q. 24. Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

Ans. Anhydrous $FeCl_3$, $SnCl_4$, BF_3, etc.

Q. 25. Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms ? Illustrate your answer by taking one example.

Ans. For preparing alkanes containing odd number of carbon atoms, a mixture of two alkyl halides has to be used. These two alkyl halides may react in three different ways producing a mixture of three alkanes instead of desired alkane. For example, Wurtz reaction between bromoethane and 1-bromopropane give the following three alkanes instead of a single alkane of odd number of C—atoms.





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NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 141*

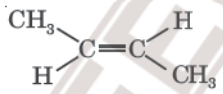
Q. 1. Why do alkenes prefer to undergo electrophilic addition reactions while arenes prefer electrophilic substitution reactions ? Explain.

Ans. Due to the presence of π-electron cloud above and below the plane of alkenes and arenes, these are electron rich molecules and therefore, provide sites for the attack of electrophiles. Hence, they undergo electrophilic reactions. The alkenes undergo electrophilic addition reactions because alkenes are unsaturated molecules. For example,

Addition product

Arenes, on the other hand, cannot undergo electrophilic addition reactions. This is because benzene has a large resonance energy of 150.4 kJ mol^{-1}. During electrophilic addition reaction, two new σ-bonds are formed but the aromatic character of benzene gets destroyed and therefore, resonance energy of benzene ring is lost. Hence, electrophilic addition reactions of arenes are not energetically favourable. Arenes, in contrast undergo electrophilic substitution reactions in which σ C – H bond is broken and new σ C – X bond is formed. The aromatic character of benzene ring is not destroyed and benzene retains its resonance energy. Hence, arenes undergo electrophilic substitution reactions.

Q. 2. Alkynes on reduction with sodium in liquid ammonia form trans alkenes. Will the butene thus formed on reduction of but-2-yne show the geometrical isomerism ?

Ans. $CH_3—C \equiv C—CH_3 \xrightarrow[196–200K]{Na,\ liq.\ NH_3}$ 

But–2–yne

trans but-2-ene

But-2-ene is capable of showing geometrical isomerism.

Q. 3. Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

Ans. Rotation around C – C single bond is not completely free and it is restricted due to repulsions between the electron clouds of C – H bonds in the adjacent carbon atoms. Therefore, ethane exists in infinite number of conformations. Out of these, two extreme conformations are staggered and eclipsed. *Refer Text Page 23.*

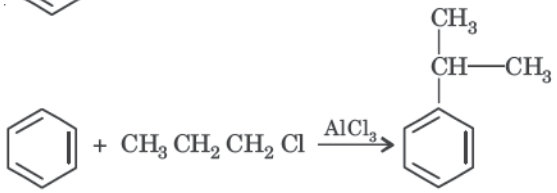
Q. 4. Draw Newman and Sawhorse projections for the eclipsed and staggered conformations of ethane. Which of these conformations is more stable and why ?

Ans. *Refer Text Page 24.*

Q. 5. The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is 430.5 kJ mol^{-1}, 363.7 kJ mol^{-1} and 296.8 kJ mol^{-1} respectively. What will be the order of reactivity of these halogen acids ?

Ans. The bond dissociation enthalpy decreases in the order. HCl > HBr > HI, therefore, the order of reactivity is in the reverse order i.e., HI > HBr > HCl.

Q. 6. What will be product obtained as a result of following reaction and why?

Ans. 

Isopropyl benzene

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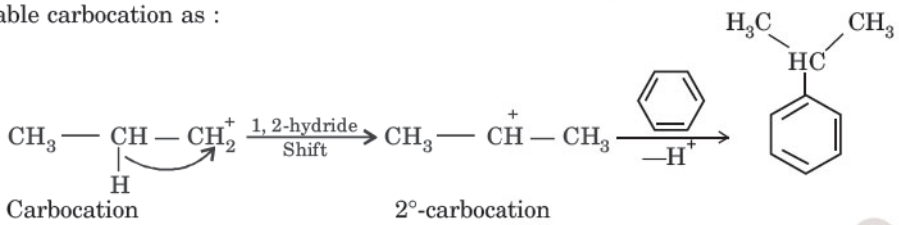
Propyl chloride forms carbocation, $CH_3 - CH_2 - CH_2^+$ with anhydrous $AlCl_3$ which is less stable. This rearranges to a more stable carbocation as :



1° Carbocation 2°-carbocation

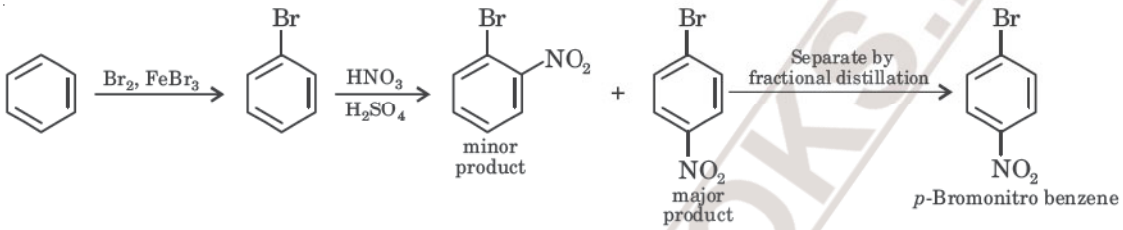
Therefore, it forms isopropyl benzene.

Q. 7. How will you convert benzene into :

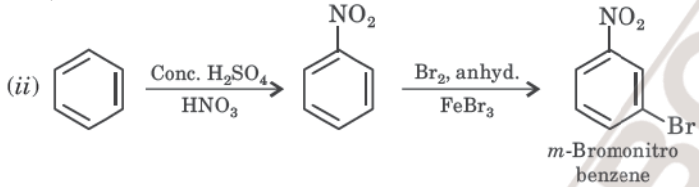
(*i*) *p*–nitrobromobenzene

(*ii*) *m* – nitrobromobenzene

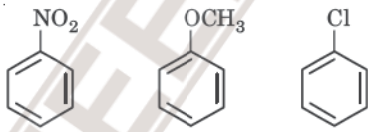
Ans. (*i*)



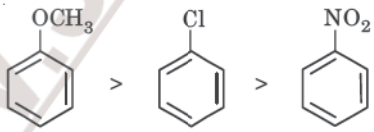
(*ii*)



Q. 8. Arrange the following set of compounds in the order of decreasing reactivity with an electrophile. Give reason.



Ans. The +R effect of $-OCH_3$ group is more than that of –Cl, whereas $-NO_2$ group has –R effect. Therefore, reactivity of the substituted benzene rings is



Q. 9. Despite their - I effect, halogens are o- and *p*-directing in haloarenes. Explain.

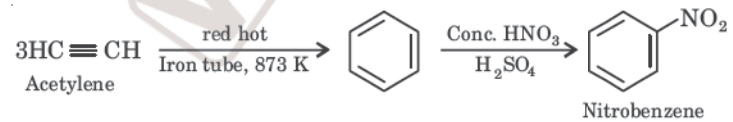
Ans. *Refer Text Page 91.*

Q.10. Why does presence of a nitro group make the benzene ring less reactive in comparison to the unsubstituted benzene ring ? Explain.

Ans. *Refer Text Page 90.*

Q. 11. Suggest a route for the preparation of nitrobenzene starting from acetylene ?

Ans.



Q. 12. Predict the major product(s) of the following reactions and explain their formation.

$$\mathbf{H_3C-CH=CH_2 \xrightarrow[HBr]{(Ph-CO-O)_2}}$$

$$\mathbf{H_3C-CH=CH_2 \xrightarrow{HBr}}$$

Ans. (*i*) $H_3C-CH=CH_2 \xrightarrow[HBr]{(Ph\ COO)_2} \underset{\text{1–Bromopropane}}{H_3C-CH_2-CH_2Br}$ (Anti-Markovnikov rule)

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(*ii*) $H_3C-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$ (Markovnikov rule)

2–Bromopropane

Reason for formation, *Refer Text* (*Page 47*).

Q. 13. Nucleophiles and electrophiles are reaction intermediates having electron rich and electron deficient centres respectively. Hence, they tend to attack electron deficient and electron rich centres respectively. Classify the following species as electrophiles and nucleophiles.

(*i*) H_3CO^- **(*ii*)** $H_3C-\overset{\overset{O}{\|}}{C}-O^-$ **(*iii*)** $\dot{Cl}$ **(*iv*)** $Cl_2C:$

(*v*) $(H_3C)_3C^+$ **(*vi*)** Br^- **(*vii*)** H_3COH **(*viii*)** $R-NH-R$

Ans. Nucleophiles : (*i*) H_3CO^- (*ii*) $H_3C-\overset{\overset{O}{\|}}{C}-O^-$ (*vii*) $CH_3-\ddot{O}-H$ (*viii*) $R-\ddot{N}H-R$

Electrophiles : (*iii*) $\dot{Cl}$ (*iv*) $Cl_2C:$ (*v*) $(H_3C)_3C^+$

Q. 14. The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1 : 3.8 : 5. Calculate the percentages of all monochlorinated products obtained from 2-methylbutane.

Ans. *Refer Solved Example 29 (Page 96).*

Q. 15. Write the structures and names of products obtained in the reactions of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane.

Ans. The following three products are formed :

(*i*) $CH_3\underset{\underset{CH_3}{|}}{CH}-CH_2\boxed{I+2Na+I}CH_2\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow[\text{reaction}]{\text{Wurtz}} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 + 2NaI$

1-Iodo-2-methylpropane (2 molecules) — 2, 5-Dimethylhexane

(*ii*) $(CH_3)_2CH\boxed{I+2Na+I}CH(CH_3)_2 \xrightarrow[\text{reaction}]{\text{Wurtz}} (CH_3)_2CH-CH(CH_3)_2 + 2NaI$

2-Iodopropane (2 molecules) — 2, 3-Dimethylbutane

(*iii*) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2\boxed{I+2Na+I}CH-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow[\text{reaction}]{\text{Wurtz}} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 + 2NaI$

1-Iodo-2-methylpropane — 2-Iodopropane — 2, 4-Dimethylpentane

Q. 16. Write hydrocarbon radicals that can be formed as intermediates during monochlorination of 2-methylpropane. Which of them is more stable ? Give reasons.

Ans. 2- Methylpropane has two sets of equivalent hydrogens marked as *a* and *b* and therefore, gives two radicals I and II

$CH_3-\underset{\underset{\dot{}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longleftarrow CH_3-\overset{\overset{a\ CH_3}{|}}{\underset{\underset{a}{|}}{\overset{b}{CH}}}-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-\dot{C}H_2$

I — II

Radical I is more stable than radical II because it is tertiary while radical II is primary. It is also stabilized due to hyperconjugation (nine structures).

Q. 17. An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.

Ans. $H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2X \xrightarrow{Na,\ ether} H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2, 5-Dimethylhexane

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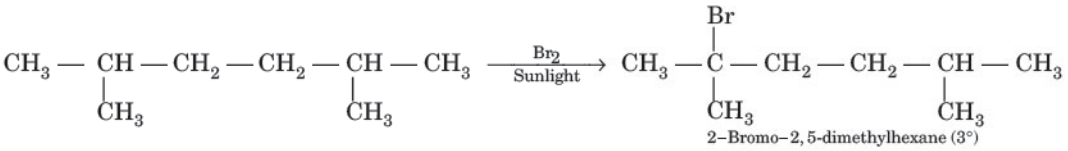
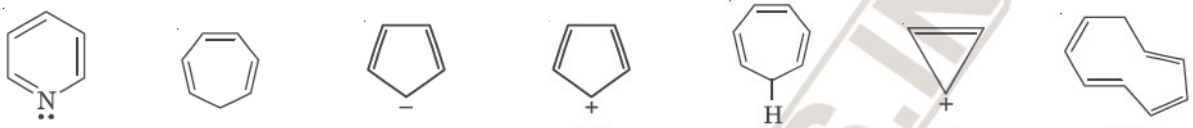


Q. 18. The ring systems having following characteristics are aromatic.

(*i*) Planar ring containing conjugated π bonds.

(*ii*) Complete delocalisation of the π-electrons in ring system i.e. each atom in the ring has unhybridised *p*-orbital, and

(*iii*) Presence of $(4n + 2)$ π-electrons in the ring where *n* is an integer ($n = 0, 1, 2, ...$) [Huckel rule]. Using this information classify the following compounds as aromatic/non-aromatic.



Ans. A = Planar ring, all atoms (C and N) of the ring are sp^2 hybridised. It has 6 delocalised π electrons and follows Huckel rule. Therefore, it is aromatic.

B = Has 6 π electrons, but the delocalisation stops at sp^3 hybridised CH_2 – carbon. Therefore, it is not aromatic.

C = 6 delocalised π electrons (4 π electrons of the two double bonds and 2 unshared electrons on negatively charged carbon) in a planar ring, follows Huckel's rule. It is aromatic.

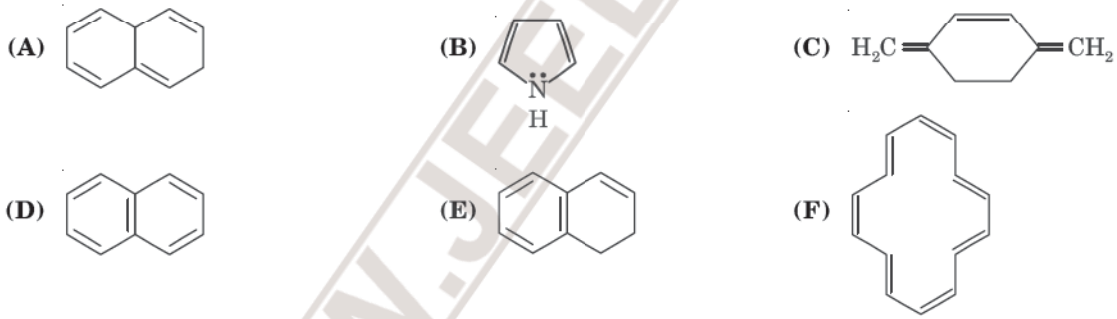
D = Has only 4 delocalised π-electrons. It is non-aromatic.

E = 6 delocalised π-electrons follows Huckel's rule. π electrons are in sp^2 hybridised orbitals, conjugation all over the ring because of positively charged carbon. The ring is planar. Therefore, it is aromatic.

F = Follows Huckel's rule, has 2 π electrons i.e., $(4n + 2)$ π-electrons where $(n = 0)$, delocalised π-electrons. Therefore, it is aromatic.

G = 8 π electrons, does not follow Huckel's rule i.e., $(4n + 2)$ π-electrons rule. It is not aromatic.

Q. 19. Which of the following compounds are aromatic according to Huckel's rule ?



Ans. A = Has 8π electrons, does not follow Huckel rule. The orbitals of one carbon atom are not in conjugation. Therefore, it is not aromatic.

B = Has 6 π delocalised electrons. Therefore, it is aromatic.

C = Has 6 π electrons in conjugation but not in the ring. Therefore, it is not aromatic.

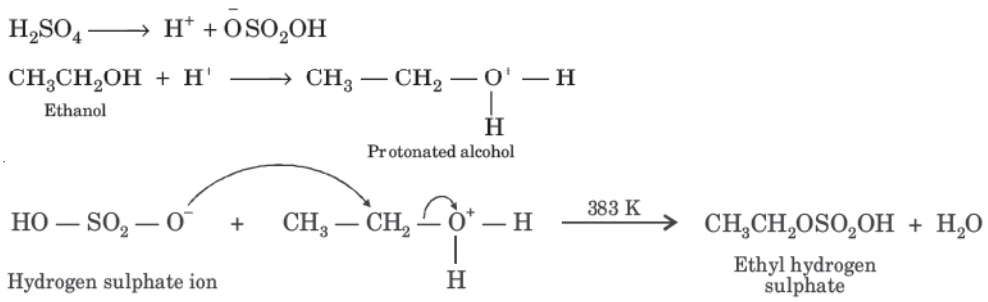
D = Has 10 π electrons, all the C-atoms are sp^2 hybridised, the ring is planar. Therefore, it is aromatic.

E = Has 8 π electrons, out of 8 π electrons it has delocalised 6 π electrons in one six membered planar ring, which follows Huckel's rule. Therefore, it is aromatic.

F = Has 14 π electrons which are in conjugation and are present in a ring. Therefore, it is aromatic if ring is planar.

Q. 20. Suggest a route to prepare ethyl hydrogen sulphate ($CH_3—CH_2—OSO_2—OH$) starting from ethanol (C_2H_5OH).

Ans. Whehanol is heated with conc. H_2SO_4 at 383 K, ethyl hydrogen sulphate is formed.



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Long Answer Questions carrying 5 marks

Q. 21. An alkyl halide $C_5H_{11}Br$ (A) reacts with ethanolic KOH to give an alkene 'B', which reacts with Br_2 to give a compound 'C', which on dehydrobromination gives an alkyne 'D'. On treatment with sodium metal in liquid ammonia one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight chain alkane. Identify A, B, C and D. Give the reactions involved.

Ans. *Refer Solved Example 33 (Page 98).*

Q. 22. 896 mL of a hydrocarbon 'A' having carbon 87.80% and hydrogen 12.19% weighs 3.28g at STP. Hydrogenation of 'A' gives 2-methylpentane. Also 'A' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone 'B' having molecular formula $C_6H_{12}O$. The ketone 'B' gives a positive iodoform test. Find the structure of 'A' and give the reactions involved.

Ans. *Refer Solved Example 44 (Page 103).*

Q. 23. An unsaturated hydrocarbon 'A' adds two molecules of H_2 and on reductive ozonolysis gives butane - 1, 4-dial, ethanal and propanone. Give the structure of 'A', write its IUPAC name and explain the reactions involved.

Ans. *Refer Solved Example 34 (Page 99).*

Q. 24. In the presence of peroxide addition of HBr to propene takes place according to anti-Markovnikov's rule but peroxide effect is not seen in the case of HCl and HI. Explain.

Ans. Anti-Markovnikov rule or peroxide effect is followed only in case of addition of HBr and not in case of HCl and HI. *Refer Text Page (Page 47-48).*

QUICK MEMORY TEST

A. Say True or False

1. The boiling point of 2, 3-dimethylbutane is higher than that of 2, 2-dimethylbutane.
2. Staggered conformation of ethane is more stable than eclipsed conformation.
3. Cyclohexane mainly exists in boat conformation.
4. The electrolysis of potassium succinate gives acetylene.
5. Bromine water can be used to distinguish between ethene and ethyne.
6. Moist ethene can be dried by passing it through conc. H_2SO_4.
7. Butan-1-ol reacts with conc. H_2SO_4 to give but-2-ene.
8. Propyne is less acidic than acetylene.
9. Nitration of nitrobenzene gives mainly *m*-dinitro benzene.
10. Chlorobenzene on reduction with Ni-Al alloy/NaOH give toluene.

B. Complete the missing links

1. All the carbon atoms in benzene are ..... hybridised.
2. When ..... is passed through red hot iron tube at 873 K, benzene is formed.
3. Propyne on ozonolysis gives ..... .
4. The reaction of ethene with bromine is ..... reaction.
5. The addition of HBr to propene in the presence of peroxides follows ..... rule.
6. The alkaline potassium permanganate solution is known as ..... .
7. The chain isomer of pent-1-yne is ..... .
8. Alkynes are ..... acidic than alkenes.
9. 2-Butyne on catalytic reduction with Lindlar's catalyst gives mainly ..... product.
10. Electrolysis of potassium fumarate gives ..... .

C. Choose the correct alternative

1. Cycloheptatrienyl cation *obeys / does not obey* Huckel rule.
2. The electrophile in sulphonation of benzene is SO_3/ $H_3SO_4^+$.
3. Nitration of bromobenzene or bromination of nitrobenzene give the *same / different* bromonitro benzene.
4. Nitration of benzene is *electrophilic / nucleophilic* substitution reaction.
5. Hydration of acetylene gives *ethanal / ethanol* .
6. But-2-yne *can / cannot* react with Tollen's reagent.
7. Chloroform on heating with silver powder gives *ethyne / ethene* .
8. Ethyne an ozonolysis gives *ethylene glycol / glyoxal*.
9. *Cis*-1, 2-dichloroethene has *less / more* dipole moment than *trans*-1, 2-dichloroethene.
10. Sodium propanoate on heating with soda lime gives *ethane / propane*.

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Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. True
3. **False :** Cyclohexane exists mainly in the chair form.
4. **False :** It gives ethylene.
5. False
6. False
7. True
8. True
9. True
10. **False :** Benzene is formed.

B. Complete the missing links

1. sp^2
2. ethyne
3. 2-oxopropanal
4. electrophilic addition
5. anti Markovnikov's
6. Baeyer's reagent
7. 3-methylbut-1-yne
8. more
9. cis
10. acetylene

C. Choose the correct alternative

1. obeys
2. SO_3
3. different
4. electrophilic
5. ethanal
6. cannot
7. ethyne
8. glyoxal
9. more
10. ethane.

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Explain : $CH_2{=}CH^-$ is more basic than $HC{\equiv}C^-$.

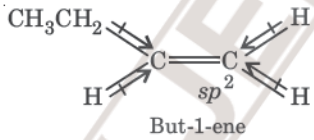
Ans. $CH_2{=}CH^-$ is a conjugate base of the acid $H_2C{=}CH_2$ while $HC{\equiv}C^-$ is a conjugate base of acid $HC{\equiv}CH$. We know that stronger the acid, weaker is the conjugate base. Since $HC{\equiv}CH$ is stronger acid than $H_2C{=}CH_2$, therefore, its conjugate base $HC{\equiv}C^-$ is weaker than that of $H_2C{=}CH^-$. Therefore, $CH_2{=}CH^-$ is more basic than $HC{\equiv}C^-$.

Q.2. Why is cyclopropane more reactive than propane ?

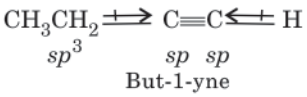
Ans. In cyclopropane, bond angle is 60° which is much less as compared to the normal tetrahedral bond angle of 109.5° for sp^3 hybridised carbon. Therefore, the molecule is very strained and hence reactive.

Q.3. Which of the two : but-1-ene or but-1-yne has larger dipole moment ? Explain.

Ans. The dipole moments of but-1-ene and but-1-yne are shown below :



But-1-ene

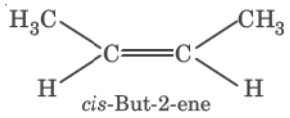


But-1-yne

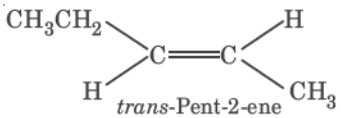
The resultant dipole moment of but-1-ene and but-1-yne is due to the dipole moment of CH_3CH_2—C and C—H bonds which oppose each other. Since a *sp*-carbon is more electronegative than a sp^2 carbon, therefore polarity of CH_3CH_2 (sp^3)—C(*sp*) bond in but-1-yne is more than that of CH_3CH_2 (sp^3)—C(sp^2) bond in but-1-ene. Thus, the dipole moment of but-1-yne is more than that of but-1-ene.

Q.4. What alkyne would you start with and what reagents would you use to prepare :

(*i*) *cis*-but-2-ene (*ii*) *trans*-pent-2-ene

Ans. (*i*) $CH_3CH_2C{\equiv}CH \xrightarrow[\text{Lindlar's catalyst}]{H_2}$ 

cis-But-2-ene

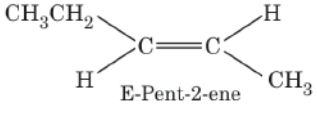
(*ii*) $CH_3CH_2C{\equiv}CCH_3 \xrightarrow[NH_3]{Na}$ 

trans-Pent-2-ene

Q.5. Show steps to prepare (E)-pent-2-ene from acetylene.

Ans. $HC{\equiv}CH \xrightarrow{NaNH_2} HC{\equiv}C^-Na^+ \xrightarrow{CH_3CH_2Br} CH_3CH_2C{\equiv}CH \xrightarrow{NaNH_2} CH_3CH_2C{\equiv}C^-Na^+$

Acetylene

$CH_3CH_2C{\equiv}C^-Na^+ \xrightarrow{CH_3Br} CH_3CH_2C{\equiv}CCH_3 \xrightarrow[\text{liq. } NH_3]{Na}$ 

E-Pent-2-ene

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Q.6. When ethene gas is passed through an aqueous solution containing bromine and sodium chloride, three products are formed. Predict the products.

Ans. $CH_2=CH_2 + Br-Br \longrightarrow H_2C(Br^+)-CH_2 + Br^-$

$H_2C(Br^+)-CH_2 \xrightarrow{H_2O} Br-CH_2CH_2OH_2^+ \xrightarrow{-H^+} BrCH_2CH_2OH$

$H_2C(Br^+)-CH_2 \xrightarrow{Br^-} BrCH_2CH_2Br$

$H_2C(Br^+)-CH_2 \xrightarrow{Cl^-} BrCH_2CH_2Cl$

Q.7. When 3, 3-dimethylbutan-2-ol is treated with concentrated HI, a rearrangement occurs. Name the alkyl iodide formed showing the steps of the reaction.

Ans. $CH_3-C(CH_3)(CH_3)-CH(OH)-CH_3 \xrightarrow{H-I} CH_3-C(CH_3)(CH_3)-CH(OH_2^+)-CH_3 \xrightarrow{-H_2O} CH_3-C(CH_3)(CH_3)-\overset{+}{C}H-CH_3$

3,3-Dimethylbutan-2-ol

$\xrightarrow{\text{1,2-methyl shift}} CH_3-\overset{+}{C}(CH_3)-CH(CH_3)-CH_3 \xrightarrow{I^-} CH_3-C(I)(CH_3)-CH(CH_3)-CH_3$

2-iodo-2, 3-dimethylbutane

Q.8. Write the alkenes that give the following compounds on ozonolysis :

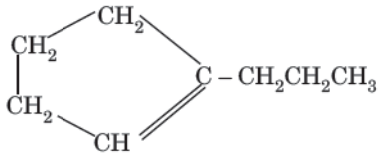
(a) $CH_3CO\,CH_2CH_3 + CH_3CHO$ ***(b)*** $HC(=O)\,CH_2CH_2CH_2\;C(=O)\,CH_2CH_2CH_3$

(c) $CH_3-C(=O)\,CH_2CH_2CH(=O) + HCH(=O) + CH_3CHO$

Ans.

(*a*) $CH_3CH_2C(=O)CH_3 + O=C(H)-CH_3 \xleftarrow[Zn,\,H_2O]{O_3} CH_3CH_2\,C(CH_3)=CHCH_3$

(*b*) $HC(=O)\,CH_2CH_2CH_2C(=O)CH_2CH_2CH_3 \xleftarrow[Zn,\,H_2O]{O_3}$



(*c*) $CH_3CCH_2CH_2CH(=O) + HCH(=O) + H_3CCH(=O) \xleftarrow[Zn,\,H_2O]{O_3} CH_3CCH_2CH_2\,CH=CH\,CH_3$ (CH_2 on the C)

or $CH_3CH=C(CH_3)CH_2CH_2CH=CH_2$

Q.9. An organic compound 'X' of molecular formula C_6H_{12} absorbs one mole of bromine to give $C_6H_{12}Br_2$. On reduction it gives 2-methylpentane, while on oxidation yields a mixture of acetic acid and isobutyric acid. Derive the structural formula of X and give its IUPAC name.

Ans. C_6H_{12} is an alkene. Oxidation of C_6H_{12} to acetic acid (CH_3COOH) and isobutyric acid ($CH_3-CH(CH_3)-COOH$) establishes its bond at C-2 as shown ahead:

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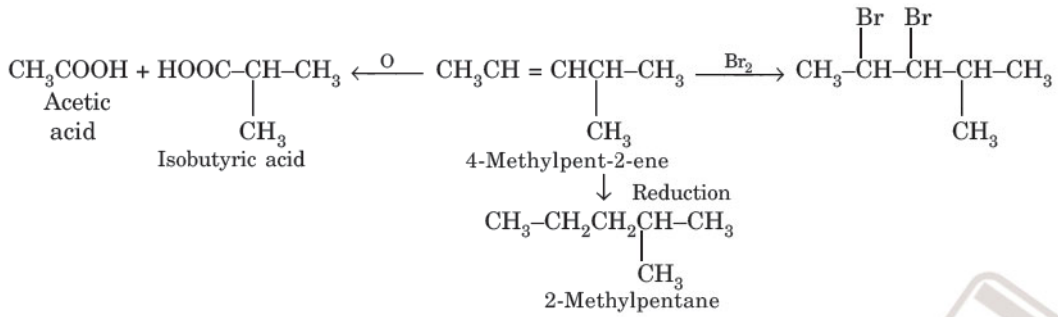
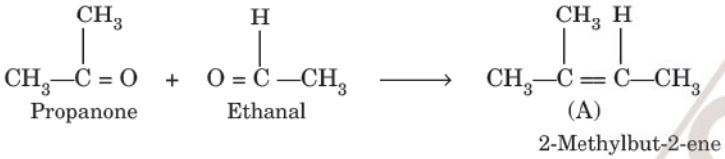


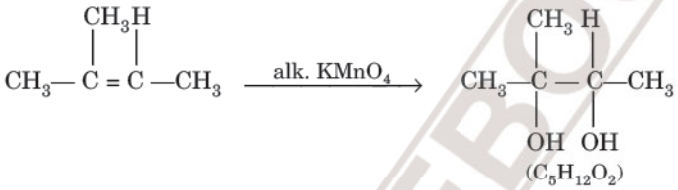
IUPAC name of X : **4-Methylpent-2-ene**

Q.10. One mole of a hydrocarbon (A) reacts with one mole of bromine giving a dibromo compound, $C_5H_{10}Br_2$. Substance (A) on treatment with cold dilute alkaline $KMnO_4$ solution forms a compound $C_5H_{12}O_2$. On ozonolysis (A) gives equimolar quantities of propanone and ethanal. Deduce the structural formula of (A).

Ans. One mole of the hydrocarbon (A) adds on one mole of bromine to form $C_5H_{10}Br_{12}$ therefore, (A) must be an alkene having molecular formula C_5H_{10}. The position of double bond is indicated by ozonolysis as

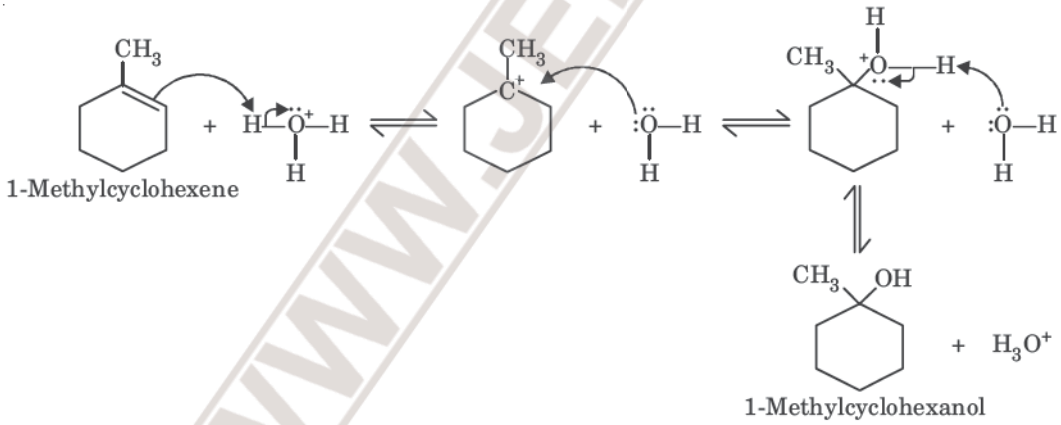


∴ The compound (A) is 2-Methylbut-2-ene. With alkaline $KMnO_4$, it forms a compound $C_5H_{12}O_2$.



Q.11. What product would you get from acid catalysed hydration of 1-methylcyclohexene ? Explain.

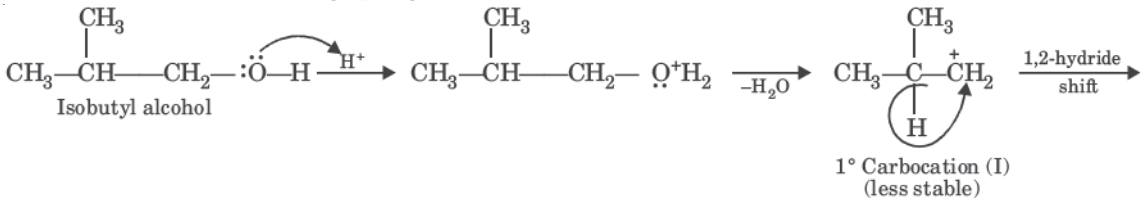
Ans. 1-Methylcyclohexanol will be formed because a 3° carbocation will be formed as an intermediate as :



Q.12. Predict the major product in the following reaction :

$$C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$$

Ans. In the presence of conc. H_2SO_4, isobutyl alcohol first forms 1° carbocation (I) which then undergoes rearrangement to the more stable 3° carbocation (II) by 1, 2-hydride shift. Carbocation (II) then reacts with benzene to form *tert*-butyl benzene as :



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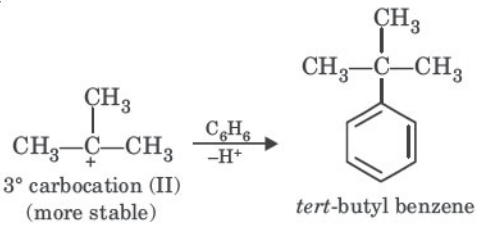
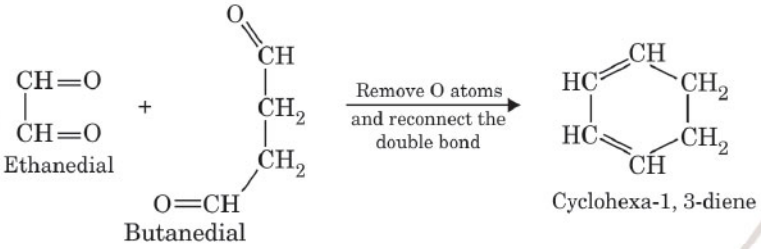
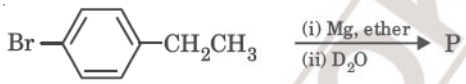


Q.13. Predict the structure of a hydrocarbon which gives one mole each of ethanedial and butanedial on ozonolysis.

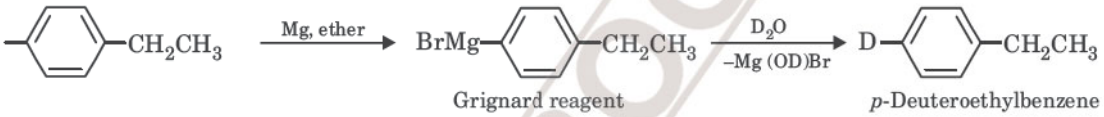
Ans.



Q.14. Predict the product of the reaction :



Ans.



Q.15. Arrange the alkenes 2-methyl but-1-ene (I), 2-methyl but-2-ene (II) and 3-methyl but-1-ene (III) in order of decreasing reactivity towards bromine.

Ans. II > I > III.

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Define conformations.
2. Name the stable conformation of cyclohexane.
3. Can ethene show conformations ? Why ?
4. What is the number of σ and π-bonds in a molecule of ethyne ?
5. Why do alkenes undergo electrophilic addition reactions ?
6. What are conjugated dienes ? Give one example.
7. What is CNG ? What is its use?
8. Name two conformations of propane.
9. Why are all C to C bond lengths in benzene equal ?
10. Why do alkynes not show geometrical isomerism ?
11. What type of hybridisation of carbon is involved in benzene ?
12. Which of the two can exhibit geometrical isomerism ? But-2-ene or But-1-ene.
13. What is Markovnikov's rule ?
14. What is Lindlar's catalyst ?
15. What is the chemical composition of teflon ?
16. How will you convert benzene into nitrobenzene ?
17. Give a chemical test to distinguish between ethane and ethene.
18. What happens when a mixture of methyl bromide and ethyl bromide is treated with dry sodium in the presence of anhydrous ether ?
19. What happens when water is added to calcium carbide ?
20. How will you prepare propyne from acetylene ?
21. Complete the reaction :

$$CH_3CH = CH_2 \xrightarrow{HBr}$$

22. What does LPG represent ?
23. Why are alkenes called olefins ?
24. How does HBr react with 1- butene ?
25. Out of ethyne and ethene, which is more acidic in nature ?

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26. Name the metal which is the constituent of Grignard reagent.

27. What is Wurtz reaction ? Give one example.

28. Give a chemical test to distinguish between but-1-yne and but-2-yne.

29. What happens when aqueous solution of sodium acetate is electrolysed ?

30. How will you convert acetylene to but-1-ane ?

31. What is peroxide effect in electrophilic addition of alkenes ?

32. Why do alkenes undergo electrophilic addition reactions ?

33. What effect does branching of an alkane have on its melting point ?

34. How is isopropyl benzene prepared from Grignard reagent ?

35. How does benzene react with fuming sulphuric acid ? Give reaction.

Short Answer Questions *carrying 2 or 3 marks*

1. What are conformations ? Discuss conformations of ethane.

2. How do you account for the formation of ethane during chlorination of methane?

3. What is meant by
(*i*) delocalisation
(*ii*) resonance energy ?

4. Discuss the molecular orbital theory for bonding in benzene.

5. Account for the order of acidity :
Acetylene > Benzene > Hexane

6. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty ?

7. What are the necessary conditions for any compound to show aromaticity ?

8. How will you explain that there exists two varieties of 1, 2- dichloroethene while there is only one variety of 1,2-dichloroethane ?

9. Explain the stability of alkenes.

10. Give one method for the preparation of each of the following :
(*i*) Ethyne (*ii*) Ethylene
(*iii*) Propyne (*iv*) Methane.

11. Why do alkenes show geometrical isomerism ?

12. What happens when
(*i*) ethyl alcohol is heated in the presence of H_2SO_4 at 443 K ?
(*ii*) ethyl bromide is heated with alcoholic KOH ?

13. How will you detect the presence of double bond in a hydrocarbon ?

14. What are substitution reactions ? Give two examples of substitution reactions of benzene.

15. Which of the following polymerises most readily and why ?
(*i*) Acetylene (*ii*) Ethene
(*iii*) Buta-1, 3-diene.

16. Write down the products and give the mechanism of the following reactions :
(*i*) $C_6H_5OH + H_2SO_4$ (conc.)
(*ii*) $C_6H_5CH_3 + HNO_3$ and H_2SO_4 (conc.)

17. Addition of HBr to propene yields 2-bromopropane while in presence of benzyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

18. How would you convert the following compounds to benzene ?
(*i*) Acetylene (*ii*) Benzoic acid
(*iii*) Hexane (*iv*) Benzene diazonium chloride.

19. How does ethylene react with :
(*i*) bromine
(*ii*) alkaline potassium permanganate
(*iii*) ozone (*iv*) hydrogen ?

20. How does acetylene react with :
(*i*) oxygen (*ii*) bromine
(*iii*) ozone (*iv*) water
(*v*) HBr.

21. How will you convert benzene into :
(*i*) bromobenzene (*ii*) benzene sulphonic acid
(*iii*) acetophenone (*iv*) toluene

22. Explain the mechanism of electrophilic addition reactions of alkenes.

23. Explain the mechanism of nitration of benzene.

24. How will you distinguish between (give one test)
(*i*) ethylene and acetylene
(*ii*) ethane and ethylene
(*iii*) But-1-yne and But-2-yne ?

25. Complete the reactions :
(*i*) $CH_3 - C \equiv CH + H_2 \xrightarrow[\text{quinoline}]{Pd,\ BaSO_4}$
(*ii*) $CaC_2 + H_2O \longrightarrow$
(*iii*) $CH_3\,CH = CHCH_3 \xrightarrow[Zn,\ H_2O]{O_3}$
(*iv*) $HC \equiv CH \xrightarrow{Alk\ KMnO_4}$
(*v*) $CH_3\,C \equiv CH \xrightarrow{hot\ KMnO_4}$

26. Give the main products of the reactions :
(*a*) $C_6H_6 \xrightarrow[H_2SO_4]{HNO_3}$
(*b*) $C_6H_5CH_3 \xrightarrow{CrO_2Cl_2}$
(*c*) $C_6H_5CH_2CH_2CH_3 \xrightarrow{Alk.\ KMnO_4}$

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(*d*) $C_6H_6 + Cl_2 \xrightarrow{\text{Sunlight}}$

(*e*) $C_6H_6 + CH_3COCl \xrightarrow{\text{Anhyd. } AlCl_3}$

27. How will you convert :

(*a*) acetylene to acetaldehyde

(*b*) ethylene to acetylene

(*c*) isopropylbromide to *n*-propylbromide

(*d*) acetic acid to methane ?

28. Write brief notes on :

(*i*) Markovnikov's rule (*ii*) Peroxide effect.

29. Which out of ethylene or propylene is more reactive to the addition of HBr ? Explain.

30. Explain the terms substitution and addition reactions ? Methane gives substitution reaction while ethylene gives addition reaction. Justify the statement giving two examples in each case.

31. Why do alkenes undergo electrophilic addition reactions ? Explain the mechanism of HBr to ethylene.

32. How do you account for acidic nature of alkynes as compared to alkenes ? Give two reactions in which acetylene behaves as an acid.

33. Discuss the general mechanism of the electrophilic substitution in benzene. What is the role played by the catalyst ?

34. Discuss the structure of benzene in terms of resonance and orbital concept.

35. Why does benzene undergo electrophilic substitution reaction instead of electrophilic addition reaction ? Discuss the mechanism of chlorination of benzene.

36. How will you convert benzene into acetophenone ? Discuss the mechanism of the reaction.

37. How is benzene converted into nitrobenzene ? Discuss the mechanism of this reaction.

38. Explain the directive influence of substituents on benzene and their effect on reactivity.

39. Explain the term polymerisation with two examples.

40. Explain the following :

(*i*) Alkynes are acidic in nature

(*ii*) Alkenes show geometrical isomerism

41. Give four important reactions of benzene and explain the mechanism of any one of these reactions.

42. Explain the mechanism of the following reactions :

(*i*) Sulphonation of benzene

(*ii*) Addition of HBr to ethene.

43. Draw the structures of six isomeric pentenes, C_5H_{10}. Specify as E or Z to each geometric isomer.

44. Write down the products of ozonolysis of 1, 2-dimethyl benzene (o-xylene). How does the result support Kekule structure for benzene ?

45. If one mole of HBr is added to the following compounds, write down the structures of the product / products expected to be formed :

(*i*) Buta-1, 3-diene (*ii*) Penta-1, 3-diene

(*iii*) Penta -1, 4-diene (*iv*) But-1-ene.

46. Write structures of all the alkenes which on hydrogenation give 2-methyl butane.

47. Which of the following polymeries most readily and why ?

(*i*) Acetylene

(*ii*) Ethene

(*iii*) Buta-1, 3-diene

48. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitution with difficulty?

49. Why do alkynes undergo addition reactions while simple alkenes do not ?

50. Why propane has only one eclipsed confirmation while butane has three? Explain.

51. Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why ?

52. Why is Wurtz reaction not preferred or preparation of alkanes containing odd number of carbon atoms ? Explain your answer by taking one example.

Long Answer Questions *carrying 5 marks*

1. What are conformations ? Discuss the different conformations of ethane. How will you account for their difference in their relative stability ?

2. Write short notes on :

(*i*) Friedel Craft reaction

(*ii*) Markovnikov's rule

(*iii*) Wurtz reaction.

3. What are alkenes ? Why do these show geometrical isomerism? Explain the mechanism of electrophilic addition reactions to alkenes.

4. Explain the structure of benzene and give its important chemical reactions.

5. Explain the mechanism of sulphonation and nitration of benzene.

6. Explain the following :

(*i*) Acidity of alkynes.

(*ii*) Conformations of propane

(*iii*) Polymerisation reactions of alkenes.

7. Discuss the following characteristics of benzene :

(*i*) Resonance

(*ii*) Aromaticity

(*iii*) Directive influence of substituents

(*iv*) Mechanism of electrophilic substitution reaction.

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Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

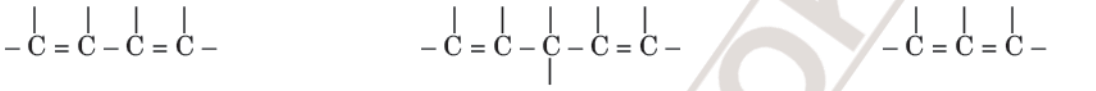
➢ ALKADIENES

The name of alkadienes is often shortened as diene. Dienes are the compounds which contain two carbon–carbon double bonds. Their general formula is similar to alkynes, C_nH_{2n-2}. Therefore, dienes are isomeric with alkynes. These are divided into three classes :

(*i*) **Conjugated dienes :** These contain two double bonds which alternate with single bonds.

(*ii*) **Isolated dienes :** These contain two double bonds that are separated by more than one single bond.

(*iii*) **Cumulated dienes or allenes :** These contain two double bonds that share a carbon atom. In these dienes one carbon atom participates in two double bonds. These three types of dienes are shown below :



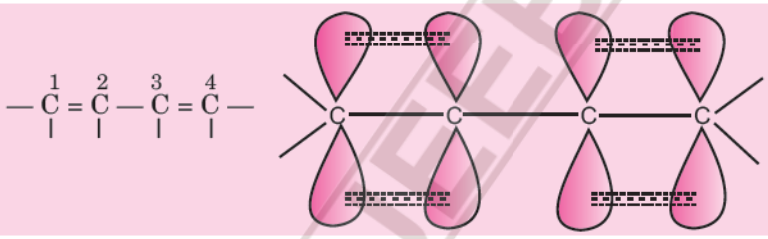
conjugated double bonds — isolated double bonds — cumulated double bonds

$CH_2 = CH - CH = CH_2$ 1, 3-Butadiene

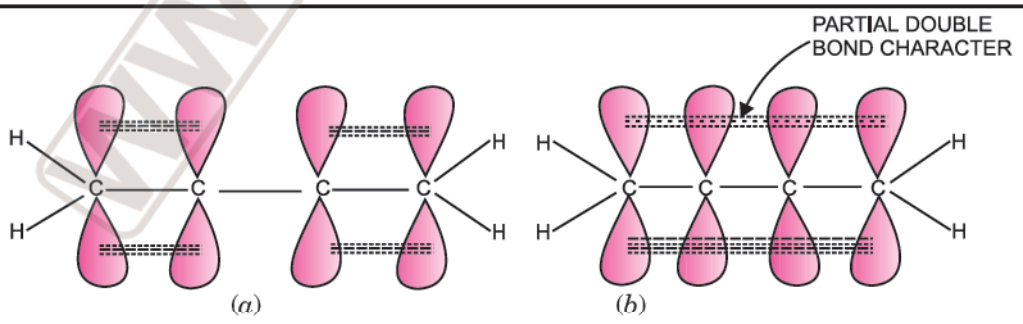
$CH_2 = CH - CH_2 - CH = CH_2$ 1, 4-Pentadiene

$CH_3CH = C = CH_2$ 1, 2-Butadiene

The stability of conjugated dienes can be explained on the basis of delocalisation of electron cloud between carbon atoms. For example consider the conjugated diene 1,3-butadiene. This may be represented as :



In 1,3–butadiene the bonds C (1)– C (2) and C(3)– C(4) are double bonds while C(2) and C(3) bond is single bond. The orbital picture shows that the π bonds are formed by the overlap of the *p* orbitals of C (1) and C(2) and *p*-orbitals of C(3) and C(4). The central carbon atoms in this molecule are close to each other and there is possibility of overlapping between *p*-orbitals of C(2) and C(3). This gives the partial double bond character to the central bond. In other words, the four π electrons of 1,3–butadiene are delocalised over all the four atoms. This delocalisation of the π electrons makes the molecule more stable.



(*a*) Overlap of *p*–orbitals in a conjugated diene to form two double bonds

(*b*) Delocalization of π-electrons.

The delocalisation of electron cloud may be represented as below :

π-Delocalised electrons

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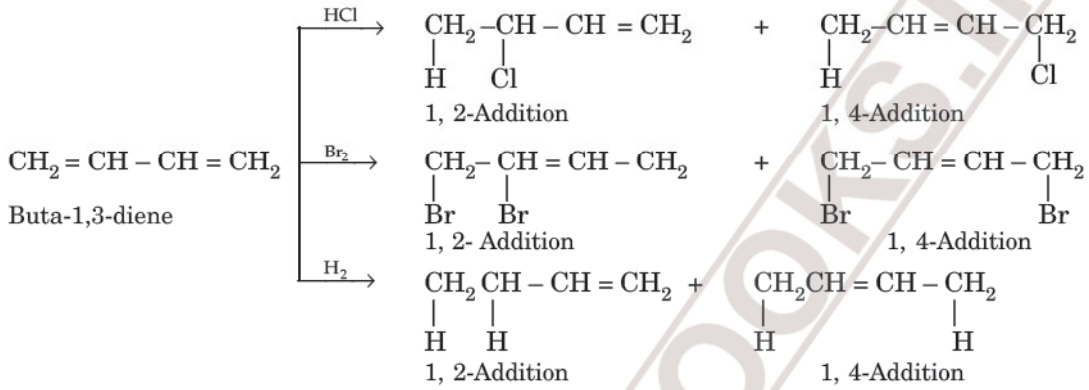
Electrophilic Addition to Conjugate Dienes

Conjugated dienes undergo electrophilic addition reactions. They show special behaviour when they react with electrophilic reagents.

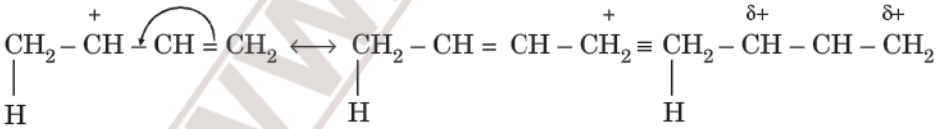
During addition to a conjugated diene, a reagent may attach itself not only to a pair of adjacent carbon atoms (**1, 2-addition**) but also to the carbon atoms at the two ends of the conjugated system (**1, 4-addition**). For example,



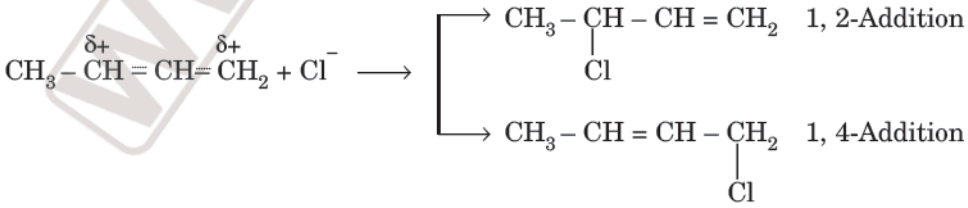
It may be noted that quite often, **1,4-addition product is the major product.** This unusual behaviour of 1,3-butadiene can be attributed to the stability of carbocation formed during the reaction.

As already discussed for electrophilic addition reactions of alkenes, the first step involves the addition of hydrogen to C – 2 to form carbocation as :

The carbocation formed is called **allylic carbocation** which means carbocation next to a double bond. Allylic carbocation gets resonance stabilised and is more stable. In second step, the chloride ion can form bond to either end of the allylic system and forms the 1, 2- and 1, 4-addition product.



Resonance stabilized allylic carbocation



The addition of HBr to 1, 3-butadiene also leads to a mixture of products. The relative amounts of 1, 2-and 1, 4-addition products depend upon the temperature of the reaction. At low temperatures, the major product is 1, 2 addition product and at higher temperature 1, 4 addition product predominates. For example, addition of HBr to 1, 3-butadiene at – 80°C gives a 80 : 20 mixture of 1, 2 and 1, 4-addition products. But at a higher temperature (40°C) gives 80% 1, 4-and 20% 1, 2-addition product. At intermediate temperatures, mixtures of intermediate compositions are formed.

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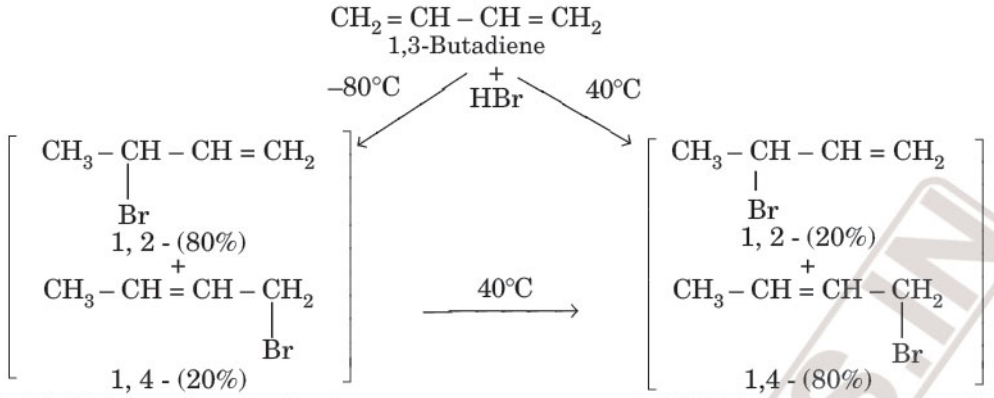


1, 2-Addition product **predominates** 1, 4-Addition product **predominates**

It is also observed that when the reaction mixture at 0°C is heated to 40°C, the composition of 80 : 20 for 1, 2 and 1, 4-product changes to 20 : 80 for 1, 2 and 1, 4 addition product.

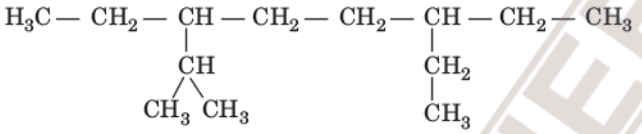
OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answers :

Alkanes

A1. The correct IUPAC name of the following alkane is



(*a*) 3, 6-Diethyl-2-methyloctane
(*b*) 3-Isopropyl-6-ethyloctane
(*c*) 3-Ethyl-5-isopropyloctane
(*d*) 5-Isopropyl-3-ethyloctane

A2. Which of the following has least boiling point ?
(*a*) *n*-Hexane (*b*) *n*-Pentane
(*c*) 2-Methylbutane
(*d*) 2,2-Dimethyl propane

A3. The chlorination of methane is an example of
(*a*) elimination reaction (*b*) substitution reaction
(*c*) addition reaction (*d*) oxidation reaction.

A4. Arrange the halogens F_2, Cl_2, Br_2, I_2, in order of their increasing reactivity with alkanes.
(*a*) $I_2 < Br_2 < Cl_2 < F_2$ (*b*) $Br_2 < I_2 < Cl_2 < F_2$
(*c*) $Br_2 < Cl_2 < F_2 < I_2$ (*d*) $F_2 < Cl_2 < Br_2 < I_2$

A5. In the reaction,

$$CH_3COOH \xrightarrow[Heat]{NaOH} X \xrightarrow{NaOH,CaO} Y;\ Y \text{ is :}$$

(*a*) CH_3CHO (*b*) CH_4
(*c*) C_2H_6 (*d*) CH_3COCH_3.

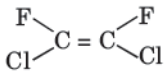
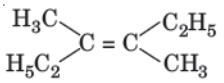
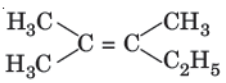
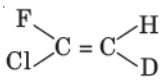
A6. An aqueous solution of compound A gives ethane on electrolysis. The compound A is :
(*a*) Ethyl acetate (*b*) Sodium acetate
(*c*) Sodium propionate (*d*) Sodium ethoxide.

A7. Arrange the following in decreasing order of their boiling points.
(A) *n*-butane (B) 2-methylbutane
(C) *n*-pentane (D) 2, 2-dimethylpropane
(*a*) A > B > C > D (*b*) B > C > D > A
(*c*) C > B > D > A (*d*) D > C > B > A

A8. Isopropyl bromide on Wurtz reaction gives
(*a*) Hexane (*b*) Propane
(*c*) 2, 3-Dimethylbutane (*d*) Neohexane

Alkenes

A9. Which of the following will not show geometrical isomerism?

(*a*) 
(*b*) 
(*c*) 
(*d*) 

A10. The ozonolysis of $(CH_3)_2C{=}C(CH_3)_2$ followed by treatment with zinc and water will give
(*a*) acetone
(*b*) acetaldehyde and acetone
(*c*) acetic acid
(*d*) formaldehyde.

A11. Ethylene reacts with Baeyer's reagent to give
(*a*) glycol (*b*) acetaldehyde
(*c*) oxalic acid (*d*) ethyl alcohol.

Answers

A1. (*a*) **A2.** (*d*) **A3.** (*b*) **A4.** (*a*) **A5.** (*b*) **A6.** (*b*) **A7.** (*c*) **A8.** (*c*) **A9.** (*c*) **A10.** (*a*) **A11.** (*a*)

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A12. A gas on passing through ammoniacal $AgNO_3$ solution does not give any precipitate but decolourises alkaline $KMnO_4$ solution. The gas may be
(*a*) C_2H_6 (*b*) C_2H_4
(*c*) C_2H_2 (*d*) C_3H_8.

A13. The compound which forms only acetaldehyde upon ozonolysis is :
(*a*) Ethene (*b*) Propyne
(*c*) But-1-ene (*d*) But-2-ene

A14. In the reaction :

$$A \xrightarrow{HBr} B \xrightarrow{\text{alc KOH}} C \xrightarrow[Zn,\ H_2O]{O_3} CH_3CHO + CO_2$$

the compound A is
(*a*) Ethylene (*b*) Acetic acid
(*c*) Propene (*d*) 1-Butene.

A15. When 3, 3-dimethyl-2-butanol is heated with H_2SO_4, the major product is
(*a*) 3, 3-dimethylbut-1-ene
(*b*) 2, 3-dimethylbut-2-ene
(*c*) 2, 3-dimethylbut-1-ene
(*d*) *cis* and *trans* isomers of product named under (*b*)

A16. Which of the following can exhibit geometrical isomerism ?
(*a*) But-2-yne (*b*) But-2-ene
(*c*) But-1-ene (*d*) Butan-2-ol.

A17. Maleic acid and fumaric acid are the forms of
(*a*) Chain isomers (*b*) Conformations
(*c*) Geometrical isomers (*d*) Optical isomers

A18. Which of the following has smallest heat of hydrogenation per mole ?
(*a*) But-1-ene (*b*) Trans- But-2-ene
(*c*) Cis- But-2-ene (*d*) Buta-1,3-diene

A19. Reaction of HBr with propene in the presence of peroxide gives
(*a*) 3-Bromopropane (*b*) alkyl bromide
(*c*) *n*-propyl bromide (*d*) isopropyl bromide

A20. Oxidation of an alkene X gives a diol; further oxidation gives a diketone. Which one of the following could be 'X' ?
(*a*) $(CH_3)_2C{=}C(CH_3)_2$ (*b*) $CH_3CH{=}C(CH_3)_2$
(*c*) $(CH_3)_2CHCH{=}CH_2$ (*d*) $C_6H_5CH{=}CHC_6H_5$

Alkynes

A21. Acetylene gas is obtained by the electrolysis of
(*a*) sodium fumarate (*b*) sodium succinate
(*c*) sodium maleate (*d*) both (*a*) and (*c*)

A22. Arrange the following carbanions in order of their decreasing stability.
(A) $H_3C-C\equiv C^-$ (B) $H-C\equiv C^-$ (C) $H_3C-CH_2^-$
(*a*) B > A > C (*b*) A > B > C
(*c*) C > A > B (*d*) C > B > A

A23. Which of the following will not react with ammoniacal solution of silver nitrate ?
(*a*) $CH_3C\equiv CH$
(*b*) $(CH_3)_2CH-C\equiv CH$
(*c*) $CH_3C\equiv CCH_3$
(*d*) $HC\equiv CH$.

A24. In the reaction :

$$HC\equiv CH \xrightarrow{NaNH_2} X \xrightarrow{CH_3I} Y \xrightarrow[H^+]{H_2O,Hg^{2+}} Z;$$

Z is :
(*a*) CH_3CHO (*b*) $CH_3CH_2CH=CH_2$
(*c*) CH_3COCH_3 (*d*) CH_3CH_2CHO

A25. Number of acidic hydrogen atoms in but-1-yne is
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4

A26. The alkyne which will react with $KMnO_4$ to give pyruvic acid is
(*a*) Ethyne (*b*) Propyne
(*c*) Butyne (*d*) Pent-2-yne

A27. Ethyne adds a molecule of methyl alcohol in the presence of alkali to give
(*a*) Acetone (*b*) Methyl vinyl ether
(*c*) Acetaldehyde (*d*) Acetic acid.

A28. Which reagent can be used to distinguish between but-1-yne and but-2-yne ?
(*a*) alc. KOH (*b*) alc. $KMnO_4$
(*c*) Br_2 water (*d*) Ag^+

A29. $C_2H_2 \xrightarrow[H_2SO_4,H_2O]{Hg^{2+}} A \xrightarrow{[O]} B;$
The compound B is
(*a*) an acid (*b*) an aldehyde
(*c*) ketone (*d*) ethanol

A30. Products of the reactions are

$$CH_3C\equiv CCH_2CH_3 \xrightarrow[373\text{-}383K]{KMnO_4,\ KOH}$$

(*a*) $CH_3COOH + CO_2$
(*b*) $CH_3COOH + HOOCCH_2CH_3$
(*c*) $CH_3CHO + CH_3CH_2CHO$
(*d*) $CH_3COOH + CH_3COCH_3$

Aromatic Hydrocarbons

A31. Benzene molecule has
(*a*) 6 σ and 6 π bonds (*b*) 16 σ and 6 π bonds
(*c*) 12 σ and 3 π bonds (*d*) 6 σ and 3 π bonds.

Answers

A12. (*b*) **A13.** (*d*) **A14.** (*c*) **A15.** (*b*) **A16.** (*b*) **A17.** (*c*) **A18.** (*b*) **A19.** (*c*) **A20.** (*d*) **A21.** (*d*)
A22. (*a*) **A23.** (*c*) **A24.** (*c*) **A25.** (*a*) **A26.** (*b*) **A27.** (*b*) **A28.** (*d*) **A29.** (*a*) **A30.** (*b*) **A31.** (*c*)

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A32. Benzene reacts with acetyl chloride in the presence of $AlCl_3$ to give
(a) acetophenone (b) toluene
(c) benzophenone (d) ethyl benzene.

A33. An aromatic compound X, C_7H_7Cl on oxidation gives an aromatic compound Y. The sodalime decarboxylation of Y gives benzene. X is
(a) *o*-chlorotoluene (b) *p*-chlorotoluene
(c) benzyl chloride (d) *m*-chlorotoluene

A34. Which of the following is less reactive than benzene towards electrophilic substitution reactions ?
(a) Nitrobenzene (b) Aniline
(c) Bromo benzene (d) Chlorobenzene

A35. In benzene, each carbon atom undergoes
(a) *sp*
(b) sp^2
(c) sp^3
(d) sp^2 and sp^3 hybridisation

A36. The number of π-bonds in naphthalene is
(a) 5 (b) 6
(c) 3 (d) 4

A37. In the reaction, $C_6H_6 + RCOCl \xrightarrow{AlCl_3} C_6H_5COR + HCl$ the attacking electrophilic is :
(a) $AlCl_2^+$ (b) R^+
(c) RCO^+ (d) $AlCl_4$

A38. *n*-Propyl chloride and benzene react in the presence of anhydrous $AlCl_3$ to form.
(a) ethyl benzene (b) methyl benzene
(c) *n*-propyl benzene (d) iso- propyl benzene

A39. Benzene reacts with C_6H_5COCl in the presence of anhydrous $AlCl_3$ to give
(a) toluene (b) naphthalene
(c) acetophenone (d) benzophenone

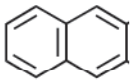
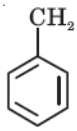
A40. The attacking reagent in electrophilic sulphonation of benzene is
(a) SO_4^{2-} (b) SO_3^{2-}
(c) SO_2 (d) SO_3

A41. In Friedel Craft reaction, anhydrous $AlCl_3$ is used. Its function is to
(a) absorb HCl (b) absorb H_2O
(c) produce electrophile (d) produce nucleophile

A42. The electrophile in nitration of benzene reaction is :
(a) NO_2 (b) NO_2
(c) NO_2^+ (d) NO

A43. Benzene can be converted into acetophenone by treating it with
(a) Acetone in the presence of HCl
(b) Acetyl chloride in the presence of $AlCl_3$
(c) Methyl chloride in the presence of $AlCl_3$
(d) Acetaldehyde in the presence of Fe

A44. Which of the following is not *o*-and *p*-directing group ?
(a) –Cl (b) $-NH_2$
(c) $-CH_3$ (d) $-NO_2$

A45. Which of the following does not obey Huckel rule ?
(a) 
(b)
(c) 
(d)

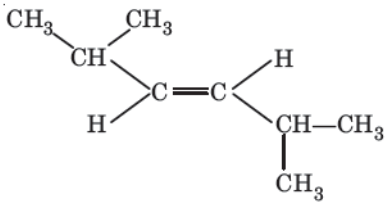
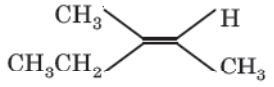
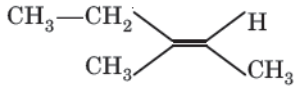
Answers

A32. (a) **A33.** (c) **A34.** (a) **A35.** (b) **A36.** (a) **A37.** (c) **A38.** (d) **A39.** (d) **A40.** (d) **A41.** (c)
A42. (c) **A43.** (b) **A44.** (d) **A45.** (b)

B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

AIPMT & Other State Boards' Medical Entrance

B1. Which of the following is not aromatic?
(a) Benzene
(b) Cyclopentadienyl cation
(c) Cyclopropenyl cation
(d) Tropylium cation
(e) Cyclopentadienyl anion *(Kerala PMT 2008)*

B2. The most stable geometrical isomer among the following is :
(a)
(b)
(c) 
(d) 
(e)  *(Kerala PMT 2008)*

Answers

B1. (b) **B2.** (a)

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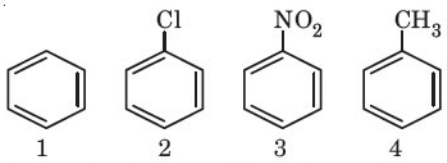
Competition File

B3. The decreasing order of reactivity towards electrophilic substitution reaction of the following compounds is :



(a) 1 > 3 > 4 > 2 (b) 4 > 1 > 3 > 2

(c) 4 > 1 > 2 > 3 (d) 4 > 2 > 1 > 3

(e) 2 > 4 > 1 > 3 *(Kerala PMT 2008)*

B4. When 2-chloro-2-methylbutane is heated with alcoholic KOH, the possible product/s is/are

a. $(CH_3)_2C{=}CHCH_3$

b. $CH_2{=}C(CH_3)CH_2CH_3$

c. $(CH_3)_2CHCH{=}CH_2$

(a) a, b, c (b) a and c

(c) b and c (d) a only

(e) a and b *(Kerala PMT 2008)*

B5. $H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH_2 + HBr \longrightarrow A.$

A (Predominantly) is :

(a) $H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_2Br$

(b) $CH_3{-}\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}CH_3$

(c) $CH_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$

(d) $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH_3$ *(CBSE PMT. 2008)*

B6. Base strength of

a. $CH_3{-}CH_2^-$ b. $H_2C{=}CH^-$ c. $H{-}C{\equiv}C^-$

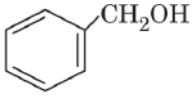
is in order of :

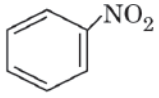
(a) b > a > c (b) c > b > a

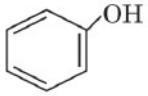
(c) a > c > b (d) a > b > c

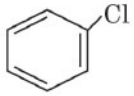
(CBSE PMT 2008)

B7. Which of the following is most reactive towards electrophilic attack?

(a) 

(b) 

(c) 

(d) 

(CBSE PMT 2008)

B8. In the hydrocarbon

$\overset{6}{CH_3}{-}\overset{5}{CH}{=}\overset{4}{CH}{-}\overset{3}{CH_2}{-}\overset{2}{C}{\equiv}\overset{1}{CH}$

The state of hybridisation of carbons 1, 3 and 5 are in following sequence :

(a) sp^2, sp, sp^3 (b) sp, sp^3, sp^2

(c) sp, sp^2, sp^3 (d) sp^3, sp^2, sp

(CBSE PMT 2008)

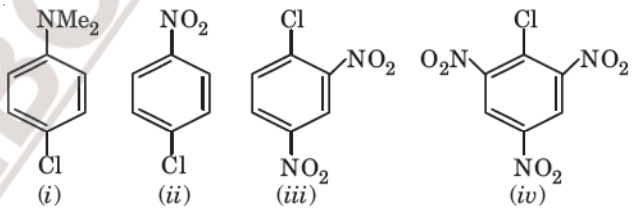
B9. Which of the following compounds will exhibit *cis-trans* isomerism ?

(a) Butanol (b) But-2-enol

(c) But-2-yne (d) toluene

(C.B.S.E.-PMT 2009)

B10. Order of reactivity towards nucleophilic substitution reaction of the compounds



(a) (i) > (ii) > (iii) > (iv)

(b) (ii) > (i) > (iii) > (iv)

(c) (iv) > (iii) > (ii) > (i)

(d) (iii) > (iv) > (ii) > (i) *(A.M.U.PMT 2009)*

B11. State of hybridisation of C_2, C_3, C_5 and C_6 of the hydrocarbon

$\overset{7}{CH_3}{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle 6\ CH_3}{\underset{|}{\overset{6}{C}}}}}{-}\overset{5}{CH}{=}\overset{4}{CH}{-}\overset{\displaystyle CH_3}{\overset{|}{\overset{3}{CH}}}{-}\overset{2}{C}{\equiv}\overset{1}{CH}$

is in the following sequence :

(a) sp^3, sp^2, sp^2 and sp

(b) sp, sp^2, sp^2 and sp^3

(c) sp, sp^2, sp^3 and sp^2

(d) sp, sp^3, sp^2 and sp^3 *(C.B.S.E.PMT 2009)*

B12. The IUPAC name of the compound having the formula $CH{\equiv}C{-}CH{=}CH_2$ is

(a) 1-butyne-3-ene (b) but-1-yne-3-ene

(c) 1-buten-3-yne (d) 3-buten-1-yne

(C.B.S.E.PMT 2009)

Answers

B3. (c) **B4.** (e) **B5.** (b) **B6.** (d) **B7.** (c) **B8.** (b) **B9.**(b) **B10.** (c) **B11.** (d) **B12.**(c)

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B13. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form :

(*a*) Chlorobenzene (*b*) Benzyl chloride
(*c*) Xylene (*d*) Toluene

(C.B.S.E.PMT 2009)

B14. When subjected to acid catalysed hydration, the order of reactivity of the alkenes;

$(CH_3)_2C = CH_2$ (I), $CH_3CH = CH_2$ (II), and $CH_2 = CH_2$ (III) is

(*a*) III > II > I (*b*) I > III > II
(*c*) I > II > III (*d*) II > I > III

(A.M.U. Med. 2010)

B15. In the eclipsed conformation of ethane, the dihedral angle between the hydrogen atoms of adjacent methyl groups is

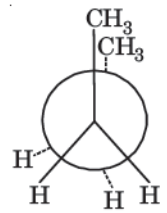
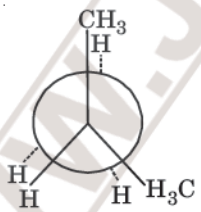
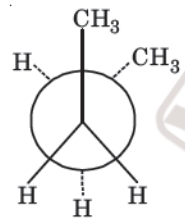
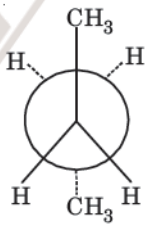
(*a*) 60° (*b*) 120°
(*c*) 0° (*d*) 180°
(*e*) 109° 28′ *(Kerala PMT 2010)*

B16. The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are :

(*a*) X = *o*- and *p*- chlorotoluene,
Y = Trichloromethyl benzene
(*b*) X = Benzyl chloride, Y = *m*- chlorotoluene
(*c*) X = Benzal chloride, Y = *o*- chlorotoluene
(*d*) X = *m*- chlorotoluene, Y = *p*- chlorotoluene

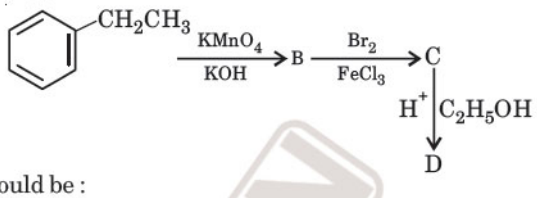
(C.B.S.E. PMT 2010)

B17. In the following the most stable conformation of *n*-butane is :

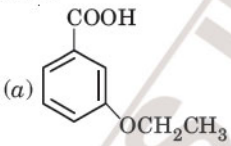
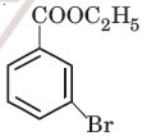
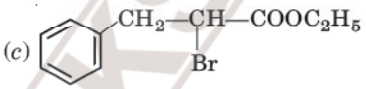
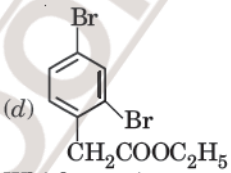
(*a*) 
(*b*) 
(*c*) 
(*d*) 

(C.B.S.E. PMT 2010)

B18. In a set of reactions, ethyl benzene yielded a product D.

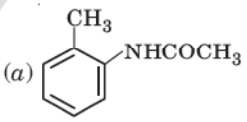
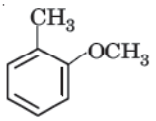
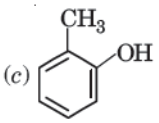
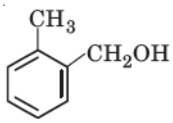


'D' would be :

(*a*) 
(*b*) 
(*c*) 
(*d*) 

(CBSE PMT 2010)

B19. Which one is most reactive towards electrophilic reagent?

(*a*) 
(*b*) 
(*c*) 
(*d*) 

(CBSE PMT 2010)

B20. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by :

(*a*) Distillation under reduced pressure
(*b*) Hydrolysis
(*c*) Oxidation
(*d*) Cracking *(CBSE PMT 2010)*

B21. A hydrocarbon contains 80% carbon. What is the empirical formula of the compound ?

(*a*) CH_2 (*b*) CH_3 (*c*) CH_4 (*d*) CH
(*e*) C_2H_3 *(Kerala PMT 2011)*

B22. When one mole of an alkene on ozonolysis produces 2 moles of propanone, the alkene is

(*a*) 3-methylbut-1-ene
(*b*) 2, 3-dimethylbut-1-ene
(*c*) 2,3-dimethylpent-2-ene
(*d*) isobutene
(*e*) 2,3-dimethylbut-2-ene *(Kerala PMT 2011)*

Answers

B13. (*d*) **B14.** (*c*) **B15.** (*c*) **B16.** (*a*) **B17.** (*d*) **B18.** (*b*) **B19.** (*c*) **B20.** (*d*) **B21.** (*b*) **B22.** (*e*)

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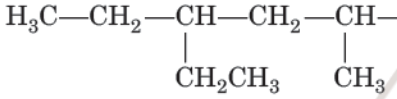
B23. Which one of the following has the lowest boiling point ?
(*a*) 2-methylbutane
(*b*) 2-methyl propane
(*c*) 2, 2-dimethyl propane
(*d*) *n*-pentane
(*e*) *n*-butane (*Kerala PMT 2011*)

B24. Reaction of hydrogen bromide with propene in the absence of peroxide is a/an
(*a*) free radical addition
(*b*) nucleophilic addition
(*c*) electrophilic substitution
(*d*) electrophilic addition
(*e*) nucleophilic substitution (*Kerala PMT 2011*)

B25. Which of the following compounds can yield only one monochlorinated product upon free radical chlorination ?
(*a*) Propane (*b*) 2, 2-Dimethylpropane
(*c*) 2-Methylpropane (*d*) *n*-Butane
(*e*) 2-Methylbutane (*Kerala PMT 2011*)

B26. Among the three conformations of butane the order of stability follows the sequence
(*a*) eclipsed > gauche > staggered
(*b*) eclipsed > staggered > gauche
(*c*) staggered > gauche > eclipsed
(*d*) gauche > staggered > eclipsed
(e) gauche > eclipsed > staggered
(*Kerala P.M.T. 2012*)

B27. The IUPAC name of the following compound

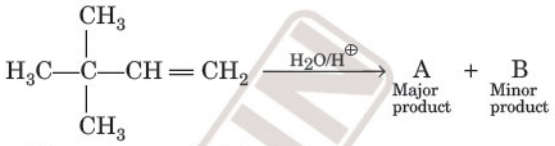


(*a*) 3-ethyl-5-methylheptane
(*b*) 5-ethyl-3-methylheptane
(*c*) 3,5-diethylhexane
(*d*) 1, 1-diethyl-3-methylpentane
(e) 1,3-diethyl-l-methylpentane
(*Kerala P.M.T. 2012*)

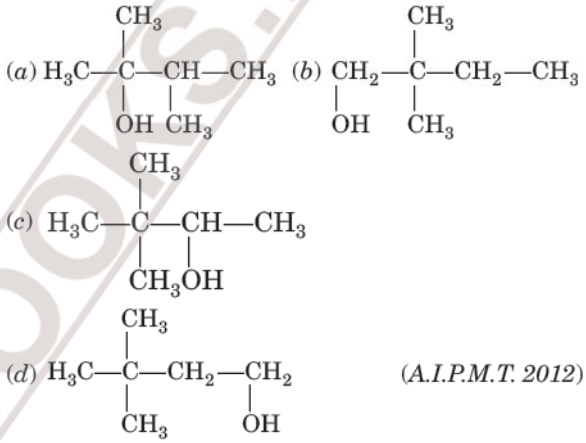
B28. Meta-directing and deactivating group in aromatic electrophilic substitution is
(*a*) $-CH_3$ (*b*) $-OH$
(*c*) $-NO_2$ (*d*) $-Cl$
(e) $-OCH_3$ (*Kerala P.M.T. 2012*)

B29. 2-Bromopentane is treated with alcoholic KOH solution. The major product formed in this reaction and the type of reaction respectively are
(*a*) pent-2-ene, β-elimination
(*b*) pent-1-ene, β-elimination
(*c*) pentan-2-ol, nucleophilic substitution
(*d*) pent-1-ene, nucleophilic substitution
(e) pent-2-ene, nucleophilic substitution
(*Kerala P.M.T. 2012*)

B30. In the following reaction



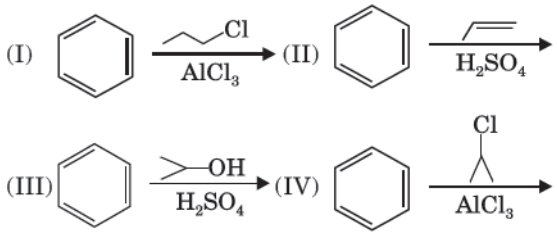
The major product is



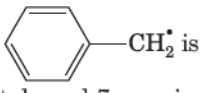
(*d*) $H_3C-C(CH_3)_2-CH_2-CH_2-OH$ (*A.I.P.M.T. 2012*)

B31. The ozonolysis of an olefin gives only propanone. The olefin is
(*a*) but-1-ene (*b*) but-2-ene
(*c*) 2, 3-dimethylbut-2-ene
(*d*) propene (*A.M.U. Med 2012*)

B32. Which of the following reactions would give isopropylbenzene as the major product ?



(*a*) I and IV only (*b*) II and III only
(*c*) II, III, IV only (*d*) All of the above
(*A.M.U. Med 2013*)

B33. The radical,  is aromatic because it has
(*a*) 7 *p*-orbitals and 7 unpaired electrons
(*b*) 6 *p*-orbitals and 7 unpaired electrons
(*c*) 6 *p*-orbitals and 6 unpaired electrons
(*d*) 7 *p*-orbitals and 6 unpaired electrons
(*NEET 2013*)

Answers

B23. (*b*) **B24.** (*d*) **B25.** (*b*) **B26.** (*c*) **B27.** (*a*) **B28.** (*c*) **B29.** (*a*) **B30.** (*a*) **B31.** (*c*) **B32.** (*d*) **B33.** (*c*)

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B34. Some meta-directing substituents in aromatic substitution are given. Which one is most deactivating?

(*a*) — COOH (*b*) $-NO_2$

(*c*) $-C \equiv N$ (*d*) $-SO_3H$

(*NEET 2013*)

B35. Arrange the following molecules in the correct order of decreasing C — C bond length:

C_2H_6, C_2H_4, C_2H_2, C_6H_6

(*a*) $C_2H_6 > C_6H_6 > C_2H_4 > C_2H_2$

(*b*) $C_2H_6 > C_2H_4 > C_6H_6 > C_2H_2$

(*c*) $C_2H_4 > C_2H_2 > C_2H_6 > C_6H_6$

(*d*) $C_2H_2 > C_6H_6 > C_2H_4 > C_2H_6$

(*e*) $C_6H_6 > C_2H_4 > C_2H_6 > C_2H_2$

(*Kerala PMT 2014*)

B36. Which of the following organic compounds has same hybridisation as its combustion product (CO_2)?

(*a*) Ethane (*b*) Ethyne

(*c*) Ethene (*d*) Ethanol

(*AI PMT 2014*)

B37. Which one of the following is an aromatic compound?

(*a*) Cyclopentadienyl cation

(*b*) Cycloheptatrienyl cation

(*c*) Cycloheptatrienyl anion

(*d*) Cycloheptatriene

(*e*) Cyclopentadiene (*Kerala PMT 2015*)

B38. n–Hexane on heating to 773 K at 10–20 atmospheric pressure in the presence of oxides of vanadium supported over alumina, yields

(*a*) 1–hexene

(*b*) 2–hexene

(*c*) benzene

(*d*) 2–methylpentane

(*e*) 2, 2-dimethylbutane (*Kerala PMT 2015*)

B39. Which one of the following is not an isomer of 3–methylbut–1–yne?

(*a*) Pent–1–yne

(*b*) Buta–1, 3–diene

(*c*) Pent–2–yne

(*d*) Penta–1, 3–diene

(*e*) 2–Methybuta–1, 3–diene (*Kerala PMT 2015*)

B40. The correct decreasing order of acidic character of hydrogen in ethane, ethene and ethyne is

(*a*) ethane > ethene > ethyne

(*b*) ethene > ethane > ethyne

(*c*) ethyne > ethane > ethene

(*d*) ethyne > ethene > ethane

(*e*) ethane > ethyne > ethene (*Kerala PMT 2015*)

B41. On ozonolysis, one molecule of a hydrocarbon produces two molecules of ethanal and one molecule of ethanedial. The hydrocarbon could be

(*a*) 1, 3–hexadiene (*b*) 1, 4–cyclohexadiene

(*c*) 1, 4–hexadiene (*d*) 2, 4–hexadiene

(*e*) 1, 3–cyclohexadiene. (*Kerala PMT 2015*)

B42. 2, 3–Dimethyl–2–butene can be prepared by heating which of the following compounds with a strong acid?

(*a*) $(CH_3)_2C = CH - CH_2 - CH_3$

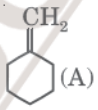
(*b*) $(CH_3)_2CH—CH_2—CH = CH_2$

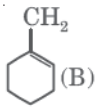
(*c*) $(CH_3)_2CH—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH = CH_2$

(*d*) $(CH_3)_3C—CH = CH_2$ (*AIPMT 2015*)

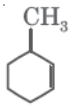
B43. In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule, to give a product 1–chloro–1–methylcyclohexane.

The possible alkene is:

(*a*)  (A)

(*b*)  (B)

(*c*) (A) and (B)

(*d*)  (*AIPMT 2015*)

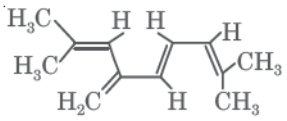
B44. The oxidation of benzene by V_2O_5 in the presence of air produces:

(*a*) benzoic acid (*b*) benzaldehyde

(*c*) benzoic anthydride (*d*) maleic anhydride

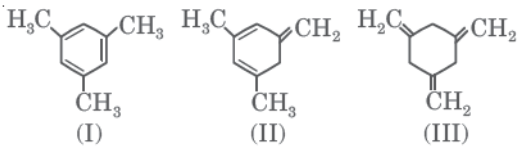
(*AIPMT 2015*)

B45. The total number of π-bond electrons in the following structure is



(*a*) 12 (*b*) 16 (*c*) 4 (*d*) 8 (*AIPMT 2015*)

B46. Given:



(I) (II) (III)

The enthalpy of hydrogenation of these compounds will be in the order as

(*a*) II > III > I (*b*) II > I > III

(*c*) I > II > III (*d*) III > II > I

(*AIPMT 2015*)

Answers

B34. (*b*) **B35.** (*a*) **B36.** (*b*) **B37.** (*b*) **B38.** (*c*) **B39.** (*b*) **B40.** (*d*) **B41.** (*d*) **B42.** (*d*)
B43. (*c*) **B44.** (*d*) **B45.** (*d*) **B46.** (*d*)

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B47. The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is
(*a*) the eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
(*b*) the staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
(*c*) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain
(*d*) the eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain.
(*NEET 2016*)

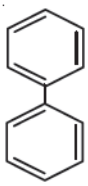
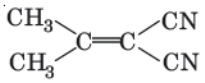
B48. Consider the nitration of benzene using mixed conc. H_2SO_4 and HNO_3. If a large amount of $KHSO_4$ is added to the mixture, the rate of nitration will be
(*a*) unchanged (*b*) doubled
(*c*) faster (*d*) slower. (*NEET 2016*)

B49. In the reaction

$$H-C\equiv CH \xrightarrow[(ii)CH_3CH_2Br]{(i)NaNH_2/liq.NH_3} X \xrightarrow[(ii)CH_3CH_2Br]{(i)NaNH_2/liq.NH_3} Y$$

(*a*) X = but–2–yne, Y = hex–2–yne
(*b*) X = but–1–yne, Y = hex–2–yne
(*c*) X = but–1–yne, Y = hex–3–yne
(*d*) X = but–2–yne, Y = hex–3–yne. (*NEET 2016*)

B50. In which of the following molecules, all atoms are coplanar?

(*a*) 
(*b*)
(*c*) 
(*d*)

(*NEET 2016*)

B51. The compound that will react most readily with gaseous bromine has the formula
(*a*) C_3H_6 (*b*) C_2H_2
(*c*) C_4H_{10} (*d*) C_2H_4 (*NEET 2016*)

B52. Which of the following can be used as the halide component for Fridel-Crafts reaction?
(*a*) Chlorobenzene
(*b*) Bromobenzene
(*c*) Chloroethene
(*d*) Isopropyl chloride (*NEET 2016*)

B53. Which one is the correct order of acidity?
(*a*) $CH\equiv CH > CH_3-C\equiv CH > CH_2=CH_2 > CH_3-CH_3$
(*b*) $CH\equiv CH > CH_2=CH_2 > CH_3-C\equiv CH > CH_3-CH_3$
(*c*) $CH_3-CH_3 > CH_2=CH_2 > CH_3-C\equiv CH > CH\equiv CH$
(*d*) $CH_2=CH_2 > CH_3-CH_3 > CH_3-C\equiv CH > CH\equiv CH$
(*NEET 2017*)

B54. With respect to the conformers of ethane, which of the following statements is true?
(*a*) Bond angle changes but bond length remains same.
(*b*) Both bond angle and bond length change.
(*c*) Both bond angle and bond length remain same.
(*d*) Bond angle remains same but bond length changes.
(*NEET 2017*)

B55. Predict the correct intermediate end product in the following reaction:

$$H_3C-C\equiv CH \xrightarrow[HgSO_4]{H_2O,H_2SO_4} \underset{(A)}{\text{intermediate}} \rightarrow \underset{(B)}{\text{product}}$$

(*a*) **A** : $H_3C-\underset{\displaystyle SO_4}{\underset{|}{C}}=CH_2$ **B** : $H_3C-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$
(*b*) **A** : $H_3C-\underset{\displaystyle OH}{\underset{|}{C}}=CH_2$ **B** : $H_3C-\underset{\displaystyle SO_4}{\underset{|}{C}}=CH_2$
(*c*) **A** : $H_3C-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$ **B** : $H_3C-C\equiv CH$
(*d*) **A** : $H_3C-\underset{\displaystyle OH}{\underset{|}{C}}=CH_2$ **B** : $H_3C-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$
(*NEET 2017*)

B56. Which of the following molecule represents the order of hybridisation sp^2, sp^2, sp, sp from left to right atoms?
(*a*) $HC\equiv C-C\equiv CH$
(*b*) $CH_2=CH-C\equiv CH$
(*c*) $CH_2=CH-CH=CH_2$
(*d*) $CH_3-CH=CH-CH_3$ (*NEET. 2018*)

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B57. Reaction of *trans* 2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces
(*a*) 2-phenylcyclopentene
(*b*) 1-phenylcyclopentene
(*c*) 3-phenylcyclopentene
(*d*) 4-phenylcyclopentene (*A.I.E.E.E. 2006*)

Answers

B47. (*b*) **B48.** (*d*) **B49.** (*c*) **B50.** (*a*) **B51.** (*a*) **B52.** (*d*) **B53.** (*a*) **B54.** (*c*) **B55.** (*d*)
B56. (*b*) **B57.** (*c*)

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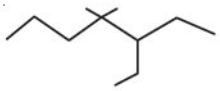
B58. The IUPAC name of  is

(*a*) 4,4-Dimethyl-5,5-diethylpentane

(*b*) 5,5-diethyl-4,4-dimethylpentane

(*c*) 3-ethyl-4,4-dimethylheptane

(*d*) 1,1-diethyl-2,2-dimethylpentane

(A.I.E.E.E. 2007)

B59. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is :

(*a*) acetophenone

(*b*) benzoic acid

(*c*) benzyl alcohol

(*d*) benzophenone. *(A.I.E.E.E. 2007)*

B60. Which of the following reactions will yield 2, 2-dibromopropane ?

(*a*) $CH_3CH{=}CHBr + HBr \longrightarrow$

(*b*) $CH{\equiv}CH + 2HBr \longrightarrow$

(*c*) $CH_3{-}CH{=}CH_2 + HBr \longrightarrow$

(*d*) $CH_3{-}C{\equiv}CH + 2HBr \longrightarrow$ *(A.I.E.E.E. 2007)*

B61. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives predominantly :

(*a*) benzyl chloride

(*b*) *o*-and *p*-chlorotoluene

(*c*) *m*-chlorotoluene

(*d*) benzoyl chloride. *(A.I.E.E.E. 2007)*

B62. Presence of a nitro group in a benzene ring :

(*a*) renders the ring basic

(*b*) deactivates the ring towards nucleophilic substitution.

(*c*) deactivates the ring towards electrophilic substitution

(*d*) activates the ring towards electrophilic substitution *(A.I.E.E.E. 2007)*

B63. An organic compound with molecular formula C_6H_{12} upon ozonolysis gave only acetone as the product. The compound is

(*a*) 2,3-dimethylbut-1-ene

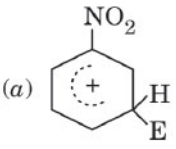
(*b*) hex-3-ene

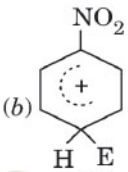
(*c*) hex-2-ene

(*d*) 2,3-dimethylbut-2-ene

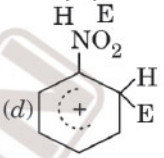
(*e*) 3-methylpent-1-ene *(Kerala PET 2008)*

B64. The electrophile, E^+ attacks the benzene ring to generate the intermediate σ-complex. Of the following, which σ-complex is of lowest energy?

(*a*) 

(*b*) 

(*c*)

(*d*) 

(AIEEE 2008)

B65. In the following sequence of reactions, the alkene affords the compound B

$CH_3CH{=}CHCH_3 \xrightarrow{O_3} A \xrightarrow{Zn} B$

The compound B is

(*a*) CH_3CHO (*b*) CH_3CH_2CHO

(*c*) CH_3COCH_3 (*d*) $CH_3CH_2COCH_3$

(AIEEE 2008)

B66. The hydrocarbon which can react with sodium in liquid ammonia is

(*a*) $CH_3CH_2C{\equiv}CCH_2CH_3$

(*b*) $CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$

(*c*) $CH_3CH_2C{\equiv}CH$

(*d*) $CH_3CH{\equiv}CHCH_3$ *(AIEEE 2008)*

B67. The treatment of CH_3MgX with $CH_3C{\equiv}C{-}H$ produces

(*a*) CH_4 (*b*) $CH_3{-}CH{=}CH_2$

(*c*) $CH_3C{\equiv}C{-}CH_3$ (*d*) $CH_3{-}CH{=}CH{-}CH_3$

(AIEEE 2008)

B68. In which of the following species, all three types of hybrid carbons are present ?

(*a*) $CH_2{=}C{=}CH_2$ (*b*) $CH_3{-}CH{=}CH{-}CH_2$

(*c*) $CH_3{-}C{\equiv}C{-}CH_2^+$ (*d*) $CH_3{-}HC{=}CH{-}CH_2^-$

(*e*) $CH_2{=}CH{-}CH{=}CH_2$ *(Kerala Engg. 2009)*

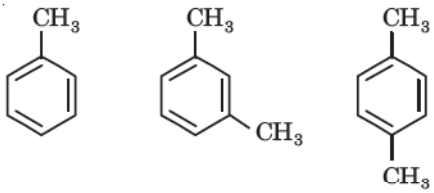
B69. Aqueous solution of sodium succinate on electrolysis gives

(*a*) $CH_3 - CH_3$ (*b*) $CH_2{=}CH_2$

(*c*) $CH \equiv CH$ (*d*) CO_2

(Orissa JEE 2010)

B70. The ease of nitration of the following three hydrocarbons follows the order



(I) (II) (III)

(*a*) II = III = I (*b*) II > III > I

(*c*) III > II > I (*d*) I = III > II *(WB JEE 2011)*

Answers

B58. (*c*) **B59.** (*b*) **B60.** (*d*) **B61.** (*b*) **B62.** (*c*) **B63.** (*a*) **B64.** (*c*) **B65.** (*a*) **B66.** (*c*) **B67.** (*a*) **B68.** (*c*) **B69.** (*b*) **B70.** (*d*)

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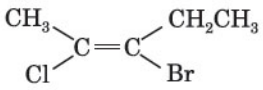
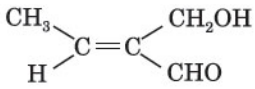
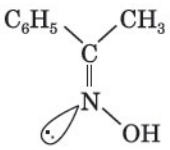
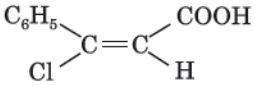
B71. The Z isomer among the following is

(*a*) 

(*b*) 

(*c*) 

(*d*)  (*A.M.U. Engg. 2011*)

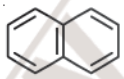
B72. When 3-phenylpropene reacts with HBr in the presence of peroxide, the major product formed is

(*a*) 2-bromo-1-phenylpropane
(*b*) 1, 2-dibromo-3-phenylpropane
(*c*) 3-(o-bromophenyl) propene
(*d*) 1-bromo-3-phenylpropane
(*e*) 3-(p-bromophenyl) propene (*Kerala P.E.T. 2011*)

B73. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of

(*a*) two ethylenic double bonds
(*b*) a vinyl group
(*c*) an isopropyl group
(*d*) an acetylenic triple bond (*A.I.E.E.E. 2011*)

B74. The non-aromatic compound among the following is

(*a*) (*b*) 

(*c*) (*d*) (*A.I.E.E.E. 2011*)

B75. The IUPAC name of is

(*a*) 4-Hydroxypentan-2-one
(*b*) 2-Hydroxypentan-4-one
(*c*) 2-Oxopentan-4-ol
(*d*) 4-Ketopentan-2-ol (*Kerala C.E.T. 2012*)

B76. The number of sigma(σ) and *pi*(π) bonds present in 1, 3, 5, 7-octatetraene respectively are

(*a*) 14 and 3 (*b*) 17 and 4
(*c*) 16 and 5 (*d*) 15 and 4
(e) 16 and 3 (*Kerala P.E.T. 2012*)

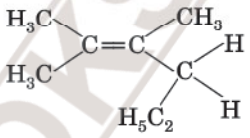
B77. When HBr adds on hex-1-ene in the presence of benzoyl peroxide, the product is

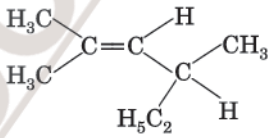
(*a*) 2-bromohexane (*b*) 2, 3-dibromohexane
(*c*) 1, 2-dibromohexane (*d*) 2, 4-dibromohexane
(e) 1-bromohexane (*Kerala P.E.T. 2012*)

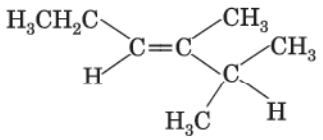
B78. 2-Hexyne gives *trans*-2-hexene on treatment with :

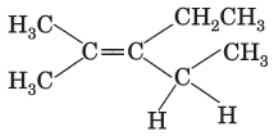
(*a*) Li/NH_3 (*b*) $Pd/BaSO_4$
(*c*) $LiAlH_4$ (*d*) Pt/H_2
(*A.I.E.E.E. 2012*)

B79. An optically active compound having molecular formula C_8H_{16} on ozonolysis gives acetone as one of the products. The structure of the compound is

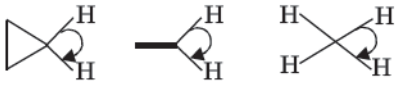
(*a*) 

(*b*) 

(*c*) 

(*d*)  (*W.B. JEE 2013*)

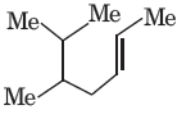
B80. The correct order of decreasing H — C — H bond angle in the following molecule is



(I) (II) (III)

(*a*) I > II > III
(*b*) II > I > III
(*c*) III > II > I
(*d*) I > III > II (*WB JEE 2014*)

B81. The IUPAC name of the following molecule is



(*a*) 5, 6-dimethylhept-2-ene
(*b*) 2, 3-dimethylhept-5-ene
(*c*) 5, 6-dimethylhept-3-ene
(*d*) 5-isopropylhex-2-ene. (*WB JEE 2014*)

Answers

B71. (*a*) **B72.** (*d*) **B73.** (*b*) **B74.** (*d*) **B75.** (*a*) **B76.** (*b*) **B77.** (*e*) **B78.** (*a*) **B79.** (*b*) **B80.** (*b*) **B81.** (*a*)

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B82. $n\text{-}C_7H_{16} \xrightarrow[10\text{-}20\ atm.]{V_2O_5,\ 500^\circ C} A \xrightarrow{Cl_2,\ hv} B$

What is B in the above reaction?

(*a*) Benzyl chloride (*b*) Benzal chloride

(*c*) Hexachlorobenzene (*d*) Benzene hexachloride

(*AMU Engg 2014*)

B83. The products obtained by ozonolysis of 2-ethylbut-1-ene are

(*a*) propanone and ethanal

(*b*) ethanal and pentan-3-one

(*c*) butanal and ethanal

(*d*) methanal and pentan-2-one

(*e*) methanal and pentan-3-one. (*Kerala PET 2014*)

B84. When but-2-yne is treated with Na in liquid ammonia

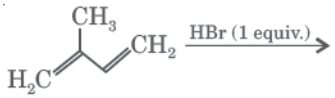
(*a*) *cis*-2-butene is obtained

(*b*) *trans*-2-butene is formed

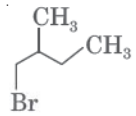
(*c*) *n*-butane is the major product

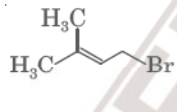
(*d*) it rearranges to but-1-yne

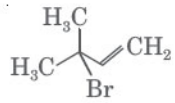
(*d*) there is no reaction. (*Kerala PET 2014*)

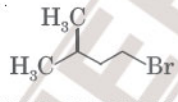
B85. 

The major product of the above reaction is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*WB JEE 2015*)

B86. Which of the following compounds will exhibit geometrical isomerism?

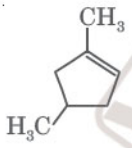
(*a*) 2–Phenyl–1–butene

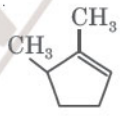
(*b*) 1, 1–Diphenyl–1–propane

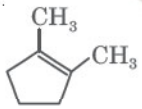
(*c*) 1–Phenyl–2–butene

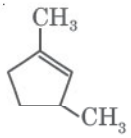
(*d*) 3–Phenyl–1–butane (*JEE Main 2015*)

B87. Which compound would give 5–keto–2–methyl hexanal upon ozonolysis

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*JEE Main 2015*)

B88. The major products obtained during ozonolysis of 2, 3-dimethyl-1-butene and subsequent reductions with Zn and H_2O are

(*a*) methanoic acid and 2-methyl-2-butanone

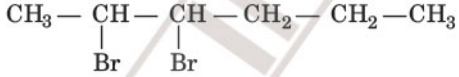
(*b*) methanal and 3-methyl-2-butanone

(*c*) methanol and 2, 3-dimethyl-3-butanone

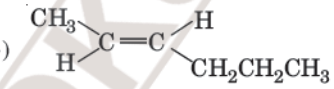
(*d*) methanoic acid and 2-methyl-3-butanone.

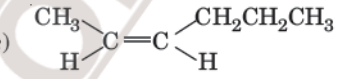
(*WB JEE 2016*)

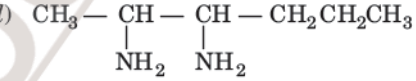
B89. Identify X in the following sequence of reactions:



(*a*)

(*b*) 

(*c*) 

(*d*) 

(*WB JEE 2016*)

B90. Predict the product (B) in the following sequence of reactions:

Ethylbenzene $\xrightarrow{KMnO_4-KOH} A \xrightarrow{H_3O^+} B$

(*a*) Benzaldehyde (*b*) Benzophenone

(*c*) Benzene (*d*) Acetophenone

(*e*) Benzoic acid (*Kerala PET 2016*)

B91. The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate:

(*a*) $CH_3–CH^+–CH_2–OH$

(*b*) $CH_3–CH^+–CH_2–Cl$

(*c*) $CH_3–CH(OH)–CH_2^+$

(*d*) $CH_3–CHCl–CH_2^+$ (*JEE Main 2016*)

B92. The isomerisation of 1-butyne to 2-butyne can be achieved by treatment with

(*a*) hydrochloric acid

(*b*) ammoniacal silver nitrate

(*c*) ammoniacal cuprous chloride

(*d*) ethanolic potassium hydroxide (*WB JEE 2017*)

B93. The reaction of propene with HBr in the presence of peroxide proceeds through the intermediate

(*a*) $H_3C—\dot{C}H—CH_3$

(*b*) $H_3C—\dot{C}H—CH_2Br$

(*c*) $H_3C—\underset{Br}{CH}—\dot{C}H_2$

(*d*) $H_3C—CH_2—\dot{C}H_2$

(*e*) none of the above. (*Kerala PET 2017*)

Answers

B82. (*a*) **B83.** (*e*) **B84.** (*b*) **B85.** (*b*) **B86.** (*c*) **B87.** (*d*) **B88.** (*b*) **B89.** (*b*) **B90.** (*e*) **B91.** (*b*) **B92.** (*d*) **B93.** (*b*)

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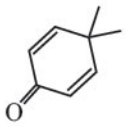
B94. Which of the following molecule is least resonance stabilized?

(a)
(b) 
(c)
(d)

(JEE Main 2017)

B95. The trans-alkenes are formed by the reduction of alkynes with:

(a) H_2 - Pd/C, $BaSO_4$ (b) $NaBH_4$
(c) Na/liq. NH_3 (d) Sn-HCl

(JEE Main 2018)

B96. What final product will form when alcoholic KOH is treated with 1,1-dichloroethane?

(a) Ethane-1,2-diol (b) Ethene
(c) Ethyne (d) Acetaldehyde

(J.K. CET 2018)

B97. Identify the following compound which exhibits gemetrical isomerism.

(a) But-2-ene (b) But-1-ene
(c) Butane (d) Iso-butane

(Karanataka CET 2018)

B98. The reagent 'X' used for the following reaction is

$$R{-}C{\equiv}C{-}R' + H_2 \xrightarrow{X} \underset{H}{\overset{R}{\diagdown}}C{=}C\underset{H}{\overset{R'}{\diagup}}$$

(a) Ni (b) Pd/C
(c) $LiAlH_4$ (d) Na/liquid NH_3

(Karanataka CET 2018)

B99. Number of constitutional isomers of alkane with formula C_6H_{14} is

(a) 3 (b) 2
(c) 5 (d) 10
(e) 8 *(Kerala PET 2018)*

B100. Phenylacetylene on treatment with $HgSO_4/H_2SO_4$, H_2O produces

(a) acetophenone (b) phenylacetaldehyde
(c) phenylacetic acid (d) 1-phenylethanol
(e) 2-phenylethanol. *(Kerala PET 2018)*

B101. Which of the following compounds are aromatic?

A B C D

(a) A,B (b) A,B,C
(c) B,C (d) B,C,D
(e) A,B,D *(Kerala PET 2018)*

B102. $CH_3{-}C{\equiv}CMgBr$ can be prepared by the reaction of

(a) $CH_3{-}C{\equiv}C{-}Br$ with $MgBr_2$
(b) $CH_3{-}C{\equiv}CH$ with $MgBr_2$
(c) $CH_3{-}C{\equiv}CH$ with KBr and Mg metal
(d) $CH_3{-}C{\equiv}CH$ with CH_3MgBr. *(W.B. JEE 2018)*

B103. The correct order for acid strength of compounds $CH{\equiv}CH$, $CH_3{-}C{\equiv}CH$ and $CH_2{=}CH_2$ is as follows:

(a) $CH_3{-}C{\equiv}CH > CH{\equiv}CH > CH_2{=}CH_2$
(b) $CH_3{-}C{\equiv}CH > CH_2{=}CH_2 > CH{\equiv}CH$
(c) $CH{\equiv}CH > CH_2{=}CH_2 > CH_3{-}C{\equiv}CH$
(d) $HC{\equiv}CH > CH_3{-}C{\equiv}CH > CH_2{=}CH_2$

(JEE Main 2019)

B104. The major product of the following reaction is :

$$CH_3CH_2\underset{Br}{CH}{-}\underset{Br}{CH_2} \xrightarrow[(ii)\ NaNH_2 \text{ in liq.}NH_3]{(i)\ KOH\ alc.}$$

(a) $CH_3CH_2C{\equiv}CH$ (b) $CH_3CH_2\underset{NH_2}{C}{-}\underset{NH_2}{CH_2}$
(c) $CH_3CH{=}C{=}CH_2$ (d) $CH_3CH{=}CHCH_2NH_2$

(JEE Main 2019)

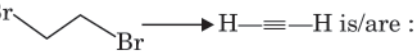
JEE (Advance) for IIT Entrance

B105. $CH_3{-}CH{=}CH_2 + NOCl \longrightarrow (A)$

Which of the following is the structure of compound A?

(a) $CH_3CHNO{-}CH_2Cl$
(b) $ON{-}CH_2{-}CH_2{-}CH_2Cl$
(c) $CH_3{-}CHCl{-}CH_2NO$
(d) $CH_2Cl{-}CHNO{-}CH_2CH_3$ *(I.I.T. 2006)*

B106. The reagents(s) for the following conversion :



(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn/CH_3OH. *(I.I.T. 2007)*

B107. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are :

(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C{\equiv}CH$
(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2\ C{\equiv}CH$
(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3\ C{\equiv}CH$
(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$ *(I.I.T. 2010)*

B108. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is(are)

(a) *sp* and sp^3 (b) *sp* and sp^2
(c) only sp^2 (d) sp^2 and sp^3

(I.I.T. J.E.E. 2012)

Answers

B94. (b) **B95.** (c) **B96.** (c) **B97.** (a) **B98.** (b) **B99.** (c) **B100.** (a) **B101.** (a) **B102.** (d) **B103.** (d) **B104.** (a) **B105.** (c) **B106.** (b) **B107.** (d) **B108.** (b)

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C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Alkanes can be obtained from carboxylic acids by
(*a*) $LiAlH_4$ (*b*) Decarboxylation
(*c*) Kolbe's electrolysis
(*d*) Clemmensen's reduction

C2. Which of the following on treatment with warm dil H_2SO_4 in the presence of $HgSO_4$ will give butan-2-one ?
(*a*) But-1-yne (*b*) But-1-ene
(*c*) But-2-yne (*d*) Pent-1-yne

C3. The molecule that will have dipole moment is
(*a*) 2,2,-Dimethylpropane
(*b*) *trans*-pent-2-ene
(*c*) *cis* hex-3-ene
(*d*) 2, 2, 3, 3-tetramethylbutane

C4. Toluene when treated with Br_2/Fe gives *p*-bromotoluene as the major product because the CH_3- group
(*a*) is *p*-directing (*b*) is *m*-directing
(*c*) activates the ring by hyperconjugation
(*d*) deactivates the ring

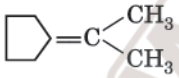
C5. But-1-ene and but-2-ene can be distinguished by
(*a*) Baeyer's reagent (*b*) hot alk. $KMnO_4$
(*c*) Reductive ozonolysis
(*d*) Tollen's reagent

C6. Which of the following can be used in Friedel Crafts acylation reactions ?
(*a*) CH_3COOCH_3 (*b*) CH_3CH_2COCl
(*c*) CH_3CH_2Cl (*d*) $(CH_3CO)_2O$

C7. Which of the following undergoes electrophilic substitution reactions faster than benzene ?
(*a*) Phenol (*b*) Aniline
(*c*) Chlorobenzene (*d*) Nitrobenzene

C8. Which of the following has almost zero dipole moment?
(*a*) *trans*-dichloroethene (*b*) *cis*-but-2-ene
(*c*) *cis*-dichloroethene (*d*) *trans*-but-2-ene

C9. Which of the following alkenes on ozonolysis give a mixture of ketones only?

(*a*) 

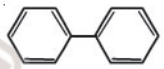
(*b*) $CH_3-CH=CH-CH_3$

(*c*) $CH_3-C(CH_3)=CH_2$

(*d*) $(CH_3)_2C=C(CH_3)_2$

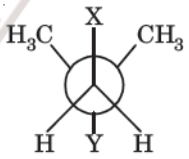
C10. Which of the following has/have aromatic character :

(*a*) (*b*)

(*c*) (*d*) 

C11. Which of the following have dipole moment.
(*a*) 2, 2-Dimethylpropane
(*b*) 2, 2, 3, 3-Tetramethylbutane
(*c*) *trans*-Pent-2-ene
(*d*) *cis*-Hex-3-ene

C12. In the Newman projection for 2, 2-dimethylbutane

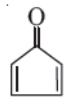
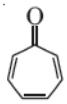


X and Y respectively be
(*a*) H and H (*b*) H and C_2H_5
(*c*) C_2H_5 and H (*d*) CH_3 and CH_3 (*IIT 2010*)

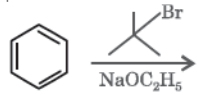
C13. Which one of the following exhibits geometrical isomerism ?
(*a*) 1, 2-dibromopropene
(*b*) 2, 3-dimethylbut-2-ene
(*c*) 2, 3-dibromobut-2-ene
(*d*) 2-methylbut-2-ene
(*e*) 2, 3-dibromobut-1-ene (*Kerala PMT 2011*)

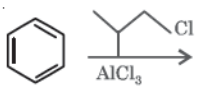
C14. Which of the following molecules, in pure form is(are) unstable at room temperature ?

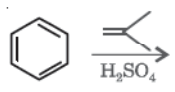
(*a*) (*b*)

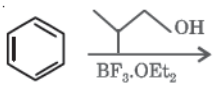
(*c*)  (*d*)  (*I.I.T. J.E.E. 2011*)

C15. Among the following, reaction(s) which gives(give) tert-butyl benzene as the major product is(are)

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*JEE Advance 2016*)

Answers

C1. (*b,c*) **C2.** (*a,c*) **C3.** (*b,c*) **C4.** (*a,c*) **C5.** (*b,c*) **C6.** (*b,d*) **C7.** (*a,b*) **C8.** (*a,d*) **C9.** (*a,d*)
C10. (*a,d*) **C11.** (*c,d*) **C12.** (*b,d*) **C13.** (*a,c*) **C14.** (*b, c*) **C15.** (*b, c, d*)

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D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage-I

Alkenes undergo a variety of oxidation reactions. With cold and neutral or alkaline $KMnO_4$, alkenes are oxidised to give vicinal diols. Oxidation with hot $KMnO_4$ undergoes cleavage of C=C bond leading to the formation of carboxylic acids, ketones and carbon dioxide depending on the nature of alkene. Reductive ozonolysis of alkenes give aldehydes or ketones.

Answer the following questions :

D1. But-2-ene on treatment with cold alk. $KMnO_4$ gives
(*a*) Butane-1, 2-diol (*b*) Butane-2, 3-diol
(*c*) Ethylene glycol (*d*) Glyoxal

D2. An alkene 'X' on treatment with hot alkaline $KMnO_4$ gives acetic acid. Alkene 'X' is
(*a*) Hex-3-ene (*b*) But-2-ene
(*c*) But-1-ene (*d*) Pent-1-ene

D3. Reductive ozonolysis of alkene 'A' gives propanone. The alkene 'A' is
(*a*) 2,3,-Dimethylbut-2-ene
(*b*) 1,4-Dimethylpent-2-ene
(*c*) 1,3-Dimethylbut-2-ene
(*d*) 2-Methylpropene

D4. 2-Methyl propene on treatment with hot alkaline $KMnO_4$ gives
(*a*) $(CH_3)_2CO$, HCOOH (*b*) $(CH_3)_2CO$, CO_2
(*c*) $(CH_3)_2CO$, CH_3CHO (*d*) CH_3CHO, CH_3CH_2CHO

Passage-II

Benzene and other aromatic hydrocarbons, though contain π-bonds, yet they behave as saturated hydrocarbons. They are stable because of delocalisation of π-cloud. These undergo electrophilic substitution reactions as :

$$C_6H_5—H + YZ \longrightarrow C_6H_5Y + HZ$$

The reactivity of aromatic hydrocarbons towards electrophilic substitution depends upon the electron density in the benzene ring.

Answer the following questions

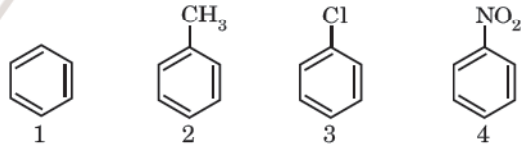
D5. Which of the following is not compatible with arenes?
(*a*) Greater stability
(*b*) Delocalisation of π-electrons
(*c*) Electrophilic addition
(*d*) Resonance

D6. In the reaction of C_6H_5Y, the major product is *m*-isomer. The group Y may be
(*a*) —COOH (*b*) —Cl (*c*) —OH (*d*) $—NH_2$

D7. The electrophile in sulphonation of benzene is
(*a*) SO_3^+ (*b*) HSO_4^- (*c*) SO_3 (*d*) $H_3SO_4^+$

D8. Which reagent cannot be used in Friedel Craft alkylation of benzene ?
(*a*) $FeCl_3$ (*b*) $SnCl_4$ (*c*) $AlCl_3$ (*d*) $LiAlH_4$

D9. The correct order of reactivity in electrophilic substitution reactions is



(*a*) 1 > 2 > 3 > 4 (*b*) 3 > 4 > 2 > 1
(*c*) 2 > 1 > 3 > 4 (*d*) 2 > 3 > 1 > 4 *(I.I.T. 2002)*

D10. Nitration of benzene undergoes in the presence of
(*a*) HCl (*b*) H_2SO_4 (*c*) NO_2^+ (*d*) HONO

Answers

Passage-I **D1.** (*b*) **D2.** (*b*) **D3.** (*a*) **D4.** (*b*)
Passage-II **D5.** (*c*) **D6.** (*a*) **D7.** (*c*) **D8.** (*d*) **D9.** (*c*) **D10.** (*b*)

Assertion Reason Type Questions

The questions given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(*b*) If both assertion and reason are CORRECT, but reason is Not the CORRECT explanation of the assertion.
(*c*) If assertion is CORRECT, but reason is INCORRECT.
(*d*) If assertion is INCORRECT, but reason is CORRECT.
(*e*) If both asseriton and reason are INCORRECT.

1. Assertion : Addition of Br_2 to but-1-ene gives two optical isomers.
Reason : The product contains one asymmetric carbon atom.

2. Assertion : Alkyl benzene is not prepared by Friedel Crafts alkylation of benzene
Reason : Alkyl halides are less reactive than acyl halides.

3. Assertion : Lactic acid shows geometrical isomerism.
Reason : It has C = C bond.

4. Assertion : Trans-but-2-ene on reaction with Br_2 gives meso-2, 3-dibromobutane.
Reason : The reaction involves syn-addition of bromine.

Answers

1. (*a*) **2.** (*a*) **3.** (*b*) **4.** (*d*)

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5. Assertion : Acetylene is more acidic than ethylene.

Reason : Acetylene has *sp* character of carbon and, therefore, more *s*-character.

6. Assertion : Propene reacts with HBr in the presence of peroxides to give 1-bromopropane.

Reason : Alkenes react with HBr in the presence of peroxides according to anti Markovnikov's rule.

7. Assertion : Terminal alkynes on oxidation with Bayer's reagent give a mixture of carboxylic acid and CO_2.

Reason : Terminal alkynes show acidic character.

8. Assertion : Nitration of nitrobenzene ives mainly m-dinitro benzene.

Reason : —NO_2 group is electron donation group.

9. Assertion : is aromatic.

Reason : It contains 4π electrons.

10. Assertion : Buta-1, 3-diene and but-1-yne can be distinguished with Tollen's reagent.

Reason : But-1-yne gives ppt. with Tollen's reagent but but-1, 3-diene does not.

11. Assertion : Toluene on Friedel Crafts methylation gives *o*-and *p*-xylene.

Reason : CH_3-group bonded to benzene ring increases electron density at *o*-and *p*-position. *(NCERT Exemplar Problem)*

12. Assertion : Among isomeric pentanes, 2, 2–dimethylpentane has highest boiling point.

Reason : Branching does not affect the boiling point. *(NCERT Exemplar Problem)*

13. Assertion : Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

Reason : The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+. *(NCERT Exemplar Problem)*

Answers

5. (*a*) **6.** (*a*) **7.** (*b*) **8.** (*c*) **9.** (*d*) **10.**(*a*) **11** (*a*) **12.** (*e*) **13.**(*a*)

Integer Type Questions

Integer Type : The answer to each of the following question is a **single-digit**-integer from 0–9.

1. The number of molecules having zero dipole moment is *trans*-but-2-ene, *cis*-pent-2-ene, *cis*-but-2-ene, propene, *trans*-1,2-dichloroethene, but-2-yne, *cis*-1,2-dichloroethene

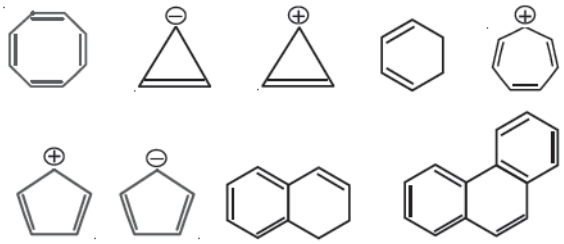
2. The number of *cis-trans* isomers with molecular formula $C_2BrClFI$ is

3. How many of the following on reductive ozonolysis will give ethanal as one of the products?

2-Methylbut-2-ene, 2-methylpropene, but-2-ene, propene, ethene, pent-2-ene, pent-3-ene, hex-3-ene

4. The number of tertiary hydrogens in 2, 3-dimethylbutane is

5. Among the following, the number of aromatic compound(s) is



(JEE Advance 2017)

Answers

1. (3) **2.** (6) **3.** (4) **4.** (2) **5.** (5)

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NCERT Exemplar Problems

Objective Questions

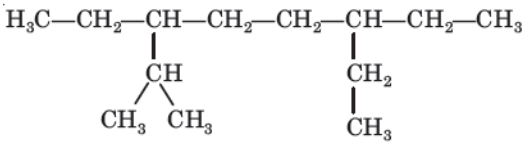
Multiple Choice Questions (Type-I)

1. Arrange the following in decreasing order of their boiling points.
(A) *n*-butane (B) 2-methylbutane
(C) *n*-pentane (D) 2,2-dimethylpropane
(*a*) A > B > C > D (*b*) B > C > D > A
(*c*) D > C > B > A (*d*) C > B > D > A

2. Arrange the halogens F_2, Cl_2, Br_2, I_2, in order of their increasing reactivity with alkanes.
(*a*) $I_2 < Br_2 < Cl_2 < F_2$ (*b*) $Br_2 < Cl_2 < F_2 < I_2$
(*c*) $F_2 < Cl_2 < Br_2 < I_2$ (*d*) $Br_2 < I_2 < Cl_2 < F_2$

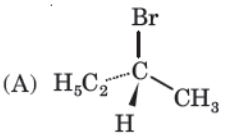
3. The increasing order of reduction of alkyl halides with zinc and dilute HCl is
(*a*) R–Cl < R–I < R–Br (*b*) R–Cl < R–Br < R–I
(*c*) R–I < R–Br < R–Cl (*d*) R–Br < R–I < R–Cl

4. The correct IUPAC name of the following alkane is

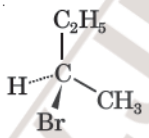


(*a*) 3,6 – Diethyl – 2 – methyloctane
(*b*) 5 – Isopropyl – 3 – ethyloctane
(*c*) 3 – Ethyl – 5 – isopropyloctane
(*d*) 3 – Isopropyl – 6 – ethyloctane

5. The addition of HBr to 1-butene gives a mixture of products A, B and C



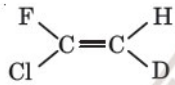
(B)



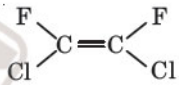
(C) $CH_3—CH_2—CH_2—CH_2—Br$
The mixture consists of
(*a*) A and B as major and C as minor products
(*b*) B as major, A and C as minor products
(*c*) B as minor, A and C as major products
(*d*) A and B as minor and C as major products

6. Which of the following will not show geometrical isomerism ?

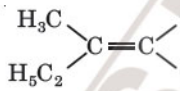
(*a*)



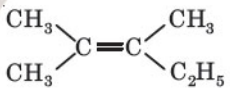
(*b*)



(*c*)



(*d*)

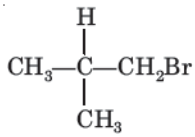


7. Arrange the following hydrogen halides in order of their decreasing reactivity with propene.
(*a*) HCl > HBr > HI (*b*) HBr > HI > HCl
(*c*) HI > HBr > HCl (*c*) HCl > HI > HBr

8. Arrange the following carbanions in order of their decreasing stability.
(A) $H_3C-C\equiv C^-$ (B) $H-C\equiv C^-$
(C) $H_3C—CH_2^-$
(*a*) A > B > C (*b*) B > A > C
(*c*) C > B > A (*d*) C > A > B

9. Arrange the following alkyl halides in decreasing order of the rate of β-elimination reaction with alcoholic KOH.

(A)



(B) $CH_3—CH_2—Br$
(C) $CH_3—CH_2—CH_2—Br$
(*a*) A > B > C (*b*) C > B > A
(*c*) B > C > A (*d*) A > C > B

10. Which of the following reactions of methane is incomplete combustion :
(*a*) $2CH_4 + O_2 \xrightarrow{Cu/523K/100\ atm} 2CH_3OH$
(*b*) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$
(*c*) $CH_4 + O_2 \longrightarrow C(s) + 2H_2O\ (l)$
(*d*) $CH_4 + 2O_2 \longrightarrow CO_2(g) + 2H_2O\ (l)$

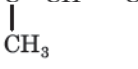
Answers

1. (*d*) **2.** (*a*) **3.** (*b*) **4.** (*a*) **5.** (*a*) **6.** (*d*) **7.** (*c*) **8.** (*b*) **9.** (*d*) **10.** (*c*)

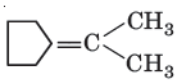
Multiple Choice Questions (Type-II)

11. Some oxidation reactions of methane are given below. Which of them is/are controlled oxidation reactions ?
(*a*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O\ (l)$
(*b*) $CH_4(g) + O_2(g) \longrightarrow C(s) + 2H_2O\ (l)$
(*c*) $CH_4(g) + O_2(g) \xrightarrow{Mo_2O_3} HCHO + H_2O$
(*d*) $2CH_4(g) + O_2(g) \xrightarrow{Cu/523\ K/100\ atm} 2CH_3OH$

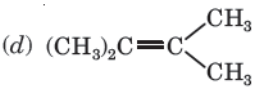
12. Which of the following alkenes on ozonolysis give a mixture of ketones only ?
(*a*) $CH_2—CH=CH—CH_3$
(*b*)



(*c*)



(*d*)



Answers

11. (*c*, *d*) **12.** (*c*, *d*)

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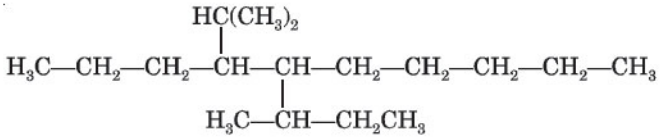
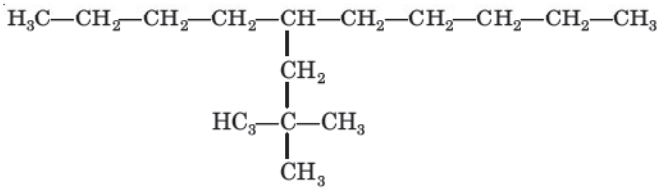
13. Which are the correct IUPAC names of the following compound ?



(*a*) 5-Butyl – 4-isopropyldecane
(*b*) 5-Ethyl – 4-propyldecane
(*c*) 5-*sec*-Butyl – 4-*iso*-propyldecane
(*d*) 4-(1-methylethyl) – 5-(1-methylpropyl)-decane

14. Which are the correct IUPAC names of the following compound ?



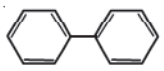
(*a*) 5 – (2′, 2′-Dimethylpropyl)-decane
(*b*) 4 – Butyl – 2,2-dimethylnonane
(*c*) 2, 2-Dimethyl – 4-pentyloctane
(*d*) 5 – *neo*-Pentyldecane

15. For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring _____.
(*a*) deactivates the ring by inductive effect
(*b*) deactivates the ring by resonance
(*c*) increases the charge density at ortho and para position relative to meta position by resonance
(*d*) directs the incoming electrophile to meta position by increasing the charge density relative to ortho and para position.

16. In an electrophilic substitution reaction of nitrobenzene, the presence of nitro group _____ .
(*a*) deactivates the ring by inductive effect.
(*b*) activates the ring by inductive effect.
(*c*) decreases the charge density at ortho and para position of the ring relative to meta position by resonance.
(*d*) increases the charge density at meta position relative to the ortho and para positions of the ring by resonance.

17. Which of the following are correct ?
(*a*) $CH_3—O—CH_2^{\oplus}$ is more stable than $CH_3—CH_2^{\oplus}$
(*b*) $(CH_3)_2CH^{\oplus}$ is less stable than $CH_3—CH_2—CH_2^{\oplus}$
(*c*) $CH_2 = CH — CH^{\oplus}$ is more stable than $CH_3 — CH_2 — CH_2^{\oplus}$
(*d*) $CH_2 = CH^{\oplus}$ is more stable than $CH_3 — CH_2^{\oplus}$

18. Four structures are given in options (*a*) to (*d*). Examine them and select the aromatic structures.

(*a*)
(*b*)
(*c*) 
(*d*)

19. The molecules having dipole moment are _____ .
(*a*) 2,2-Dimethylpropane
(*b*) *trans*-Pent-2-ene
(*c*) *cis*-Hex-3-ene
(*d*) 2, 2, 3, 3 - Tetramethylbutane.

Answers

13. (*c*, *d*) **14.** (*a*, *d*) **15.** (*a*, *c*) **16.** (*a*, *c*) **17.** (*a*, *c*) **18.** (*a*, *c*) **19.** (*b*, *c*)

Matching Type Questions

20. Match the reagent from Column I which on reaction with $CH_3—CH = CH_2$ gives some product given in Column II as per the codes given below :

Column I	Column II
(*i*) $O_3/Zn + H_2O$	(*a*) Acetic acid and CO_2
(*ii*) $KMnO_4/H^+$	(*b*) Propan - 1 - ol
(*iii*) $KMnO_4/OH^-$	(*c*) Propan - 2 - ol
(*iv*) H_2O/H^+	(*d*) Acetaldehyde and formaldehyde
(*v*) B_2H_6 / NaOH and H_2O_2	(*e*) Propane - 1,2-diol

Answers

20. (*i*) – (*d*); (*ii*) – (*a*); (*iii*) – (*e*); (*iv*) – (*c*); (*v*) – (*b*).

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21. Match the hydrocarbons in Column I with the boiling points given in Column II.

Column I	Column II
(*i*) *n*–Pentane	(*a*) 282.5 K
(*ii*) *iso*-Pentane	(*b*) 309 K
(*iii*) *neo*-Pentane	(*c*) 301 K

22. Match the following reactants in Column I with the corresponding reaction products in Column II.

Column I	Column II
(*i*) Benzene + $Cl_2 \xrightarrow{AlCl_3}$	(*a*) Benzoic acid
(*ii*) Benzene + $CH_3Cl \xrightarrow{AlCl_3}$	(*b*) Methyl phenyl ketone
(*iii*) Benzene + $CH_3COCl \xrightarrow{AlCl_3}$	(*c*) Toluene
(*iv*) Toluene $\xrightarrow{KMnO_4 / NaOH}$	(*d*) Chlorobenzene
	(*e*) Benzene hexachloride

23. Match the reactions given in Column I with the reaction types in Column II.

Column I	Column II
(*i*) $CH_2 = CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$	(*a*) Hydrogenation
(*ii*) $CH_2 = CH_2 + H_2 \xrightarrow{Pd} CH_3—CH_3$	(*b*) Halogenation
(*iii*) $CH_2 = CH_2 + Cl_2 \xrightarrow{Pd} Cl—CH_2—CH_2—Cl$	(*c*) Polymerisation
(*iv*) $3CH \equiv CH \xrightarrow[Heat]{Cu\ tube} C_6H_6$	(*d*) Hydration
	(*e*) Condensation

Answers

21. (*i*) – (*b*); (*ii*) – (*c*); (*iii*) – (*a*).
22. (*i*) – (*d*); (*ii*) – (*c*); (*iii*) – (*b*); (*iv*) – (*a*).
23. (*i*) – (*d*); (*ii*) – (*a*); (*iii*) – (*b*); (*iv*) – (*c*).

Assertion Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below :

(*a*) Both A and R are correct and R is the correct explanation of A.
(*b*) Both A and R are correct but R is not the correct explanation of A.
(*c*) Both A and R are not correct.
(*d*) A is not correct but R is correct.

24. Assertion (A) : The compound cyclooctane has the following structural formula :

It is cyclic and has conjugated 8π-electron system but it is not an aromatic compound.
Reason (R) : $(4n + 2)\ \pi$ electrons rule does not hold good and ring is not planar.

25. Assertion (A) : Toluene on Friedal Crafts methylation gives o– and *p*–xylene.
Reason (R) : CH_3 group bonded to benzene ring increases electron density at o– and *p*– position.

26. Assertion (A) : Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.
Reason (R) : The mixture of concentrated sulphuric acid and concentrated nitric acid produce the electrophile, NO_2^+.

27. Assertion (A) : Among isomeric pentanes, 2, 2-dimethylpentane has highest boiling point.
Reason (R) : Branching does not affect the boiling point.

Answers

24. (*a*) **25.** (*a*) **26.** (*a*) **27.** (*c*)

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Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A2. (*d*) : Branched chain alkanes have lower boiling point.

A5. (*b*) : $CH_3COOH \xrightarrow[\text{Heat}]{NaOH} CH_3COONa \xrightarrow[CaO]{NaOH} CH_4$

A6. (*b*) : $CH_3COONa \xrightarrow{\text{Electrolysis}} CH_3CH_3$
Sodium acetate

A8. (*c*) : $CH_3CHBr(CH_3) \xrightarrow[\text{Ether}]{Na} CH_3CH(CH_3)CH(CH_3)CH_3$
2, 3-dimethylbutane

A10. (*a*) : $(CH_3)_2C=C(CH_3)_2 \xrightarrow[(ii)\ Zn,\ H_2O]{(i)\ O_3} (CH_3)_2CO + (CH_3)_2CO$
Acetone

A11. (*a*) : $CH_2=CH_2 \xrightarrow{\text{alc. } KMnO_4} CH_2(OH)-CH_2(OH)$
Glycol

A13. (*d*) : $H_3C\,CH=CH\,CH_3 \xrightarrow[(ii)\ Zn,\ H_2O]{(i)\ O_3} 2CH_3CHO$
But-2-ene

A14. (*c*) : $CH_3CH=CH_2 \xrightarrow{HBr} CH_3CHBrCH_3 \xrightarrow{\text{alc. KOH}}$
Propene

$CH_3CH=CH_2 \xrightarrow[Zn,\ H_2O]{O_3} CH_3CHO + CO_2$

A15. (*b*) : $CH_3C(CH_3)(CH_3OH)-CHCH_3 \xrightarrow[\text{Rearrangement}]{H^+} CH_3-C(CH_3CH_3)=C-CH_3$
2,3,-Dimethylbut-2-ene

A16. (*b*) : $CH_3CH=CHCH_3$ (2-Butene) can exhibit geometrical isomerism.

A19. (*c*) : $CH_3\,CH=CH_2 \xrightarrow[\text{Peroxides}]{HBr} CH_3\,CH_2\,CH_2\,Br$
n-Propyl bromide

A23. (*c*) : Only terminal alkynes react with ammoniacal solution of $AgNO_3$.

A24. (*c*) : $HC\equiv CH \xrightarrow{NaNH_2} HC\equiv CNa \xrightarrow{CH_3I}$

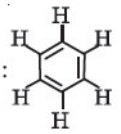
$HC\equiv C-CH_3 \xrightarrow[H^+]{H_2O,\ Hg^{2+}} H_2C=C(OH)-CH_3 \rightleftharpoons CH_3-C(=O)-CH_3$

A26. (*b*) : $CH_3C\equiv CH \xrightarrow{KMnO_4} CH_3-C(=O)-C(=O)-OH$
Propyne — Pyruvic acid

A27. (*b*) : $HC\equiv CH + CH_3OH \xrightarrow{\text{Alkali}} H_2C=CH-O\,CH_3$
Ethyne — Methyl vinyl ether

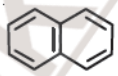
A29. (*a*) : $HC\equiv CH \xrightarrow[H^+,\ H_2O]{Hg^{2+}} CH_3CHO \xrightarrow{O} CH_3COOH$
Acid

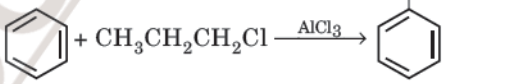
A30. (*b*) : $CH_3C\equiv CCH_2CH_3 \xrightarrow[(ii)\ \text{Hydrolysis}]{(i)\ O_3}$
$CH_3COOH + HOOCCH_2\,CH_3$

A31. (*c*) :  12σ and 3π bonds

A32. (*a*) :
Acetophenone

A33. (*c*) : $C_6H_5CH_2Cl \xrightarrow{O} C_6H_5COOH \xrightarrow[CaO]{NaOH} C_6H_6$
Benzyl chloride

A36. (*a*) :  5π bonds.

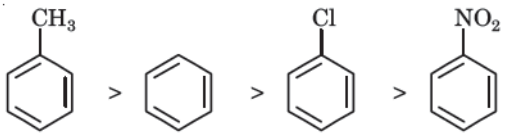
A38. (*d*) : 
Isopropyl benzene

B. *mcq from competitive examinations*

B1. (*b*): Cyclopentadienyl cation has 4π electrons. Hence it does not follow Huckel rule.

B2. (*a*): The steric repulsion of the groups makes the *cis*-isomer less stable than the *trans* isomer in which the bulky groups are far apart.

B3. (*c*): $-CH_3$ group is electron donating group and shows +I effect, $-NO_2$ group is electron withdrawing group as well as shows –M effect. –Cl group shows –I effect and is weak deactivating group. So, the order of reactivity towards electrophilic substitution reaction is



B5. (*b*) : $H_3C-C(CH_3)-CH=CH_2 + HBr \xrightarrow{+H^+}$

$H_3C-CH(CH_3)-CH^+-CH_3 \xrightarrow{\text{1,2-Hydride Shift}}$
(2°-Carbocation)

B6. (*d*): Stronger the conjugate acid, weaker will be corresponding base. Acidity of conjugate acids of given carbanions is (*c*) > (*b*) > (*a*). Therefore, the base strength is (*a*) > (*b*) > (*c*).

B7. (*c*): Hydroxy group is most activating group among the given options towards electrophilic attack.

B8. (*b*) : $\overset{sp^3}{CH_3}-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp^3}{CH_2}-\overset{sp}{C}\equiv\overset{sp}{CH}$ (1 2 3 4 5 6)

B11. (*d*) : $CH_3-C(CH_3)(CH_3)-CH=CH-CH(CH_3)-C\equiv CH$ (1 2 3 4 5 6 7)

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B14. (*c*) : Acid catalysed hydration of alkenes proceeds through formation of carbocation.

$(CH_3)_2C = CH_2 \xrightarrow{H^+} (CH_3)_2C - CH_3$
I

$CH_3CH = CH_2 \xrightarrow{H^+} CH_3CH - CH_3$
II

$CH_2 = CH_2 \xrightarrow{H^+} CH_2 - CH_3$
III

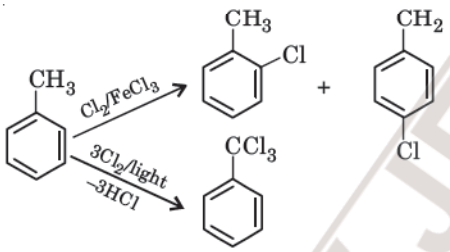
Alkene which gives more stable carbocation will be more reactive. Here alkene I gives tertiary carbocation, II gives 2° carbocation and III gives 1° carbocation. Order of stability of carbocations is 3° > 2° > 1°. Therefore, order of reactivity of alkenes is I > II > III.

B15. (*c*) : In general, the hydrogen atoms attached to sp-hybridised carbon atom are most acidic, followed by those attached to sp^2 and sp^3 hybridised carbon atoms. Therefore, order of acidity of hydrogen atoms is : alkyne > alkene > alkane

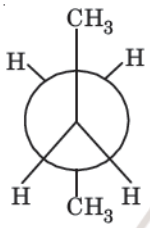
Out of ethyne and propyne, propyne is less acidic due to electron releasing – CH_3 group. Therefore, the correct order of acidity is :

$CH \equiv CH > CH \equiv C - CH_3 > CH_2 = CH_2 > CH_3 - CH_3$
(III) (IV) (II) (I)

B16. (*a*) :

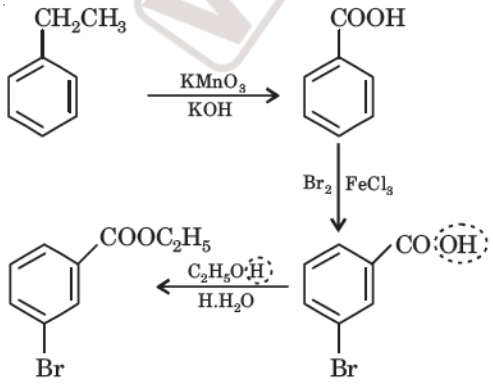


B17. (*d*) :

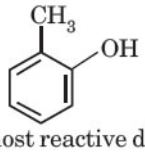


is most stable due to least repulsions between two methyl groups.

B18. (*b*) :

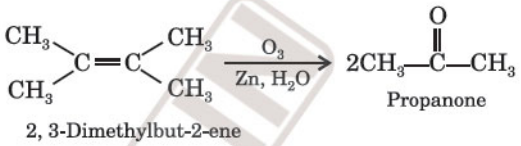


B19. (*c*) :



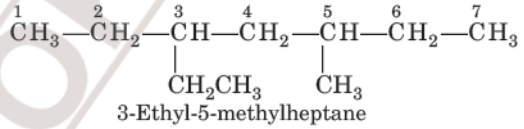
is most reactive due to the presence of electron releasing group.

B22. (*e*) :

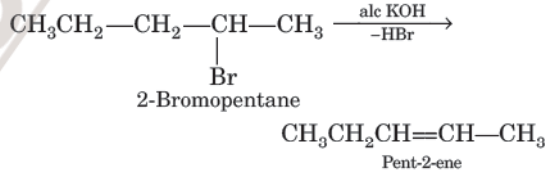


B25. (*b*) : All hydrogen atoms are equivalent in 2, 2-dimethyl propane. Therefore, it forms only one monochlorinated product.

B27. (*a*) :

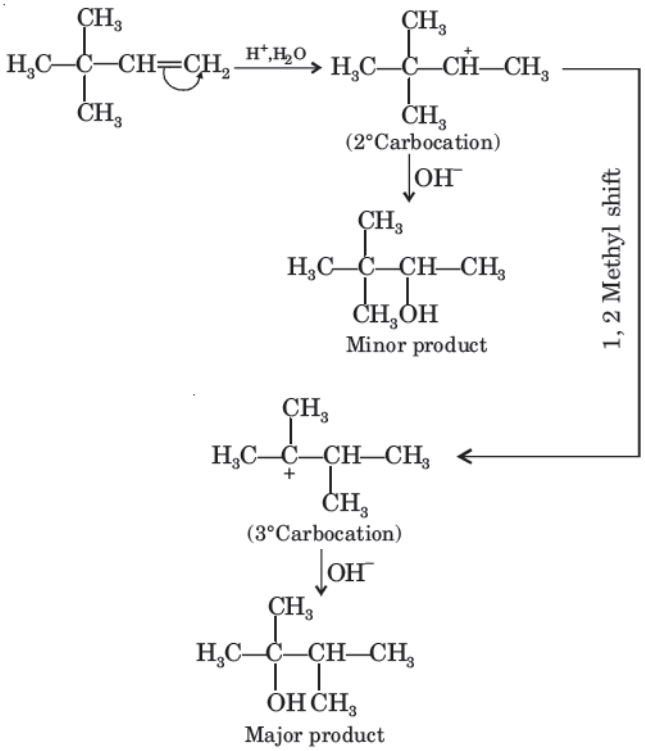


B29. (*a*) :



The reaction is known as β-elimination.

B30. (*a*) :



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B31. (*c*) : H_3C, H_3C, $C=C$, CH_3, CH_3 $\xrightarrow{\text{Ozonolysis}}$ $2CH_3C(=O)CH_3$ Propanone

or $H_3C-C(=O)CH_3 + O=C-CH_3$ (CH_3, CH_3)

$HC_3-C=CH-CH_3$ (CH_3, CH_3)

2,3-Dimethylbut-2-ene

B33. (*c*) : 6 *p*-orbitals and 6-unpaired electrons contribute to aromaticity.

B34. (*b*) : $-NO_2$ group is the most deactivating group because of strong –I and – M effect.

B35. (*a*) : Bond length decreases as

$C-C\ (C_2H_6)\ >\ C=C\ (C_2H_4)\ >\ C\equiv C\ (C_2H_2)$

sp^3 sp^2 sp

C_6H_6 (Benzene) has, bond length in between C – C and C = C and therefore correct order is

$C_2H_6\ >\ C_6H_6\ >\ C_2H_4\ >\ C_2H_2$

B36. (*b*) : Hybridisation in CO_2 : *sp*

Hybridisation in ethyne (HC ≡ CH) : *sp*

B37. (*b*)

(*a*) Planar, 4π electrons

(*b*) Planar, 6π electrons (aromatic)

(*c*) Planar, 8π electrons

(*d*) Non-planar, 6π electrons

(*e*) Non-planar, 4π electrons

B38. (*c*) : *n*-hexane $\xrightarrow[773K,\ 10–20\ atm]{V_2O_5/Al_2O_3}$ Benzene

B39. (*b*) : $CH_3-CH(CH_3)-C\equiv CH$

3–Methylbut–1–yne

(*a*) $CH_3CH_2CH_2C\equiv CH$

(*b*) $CH_2=CH-CH=CH_2$

(*c*) $CH_3CH_2C\equiv C-CH_3$

(*d*) $CH_2=CH-CH=CH-CH_3$

(*e*) $CH_2=C(CH_3)-CH=CH_2$

Isomers have same molecular formula but different structures,

(*b*) is not isomer of 2–Methylbut–1–yne.

B40. (*d*) : $HC\equiv CH > CH_2=CH_2 > CH_3-CH_3$

B41. (*d*) : $2CH_3-CH=O + OHC-CHO$

$\xleftarrow{\text{Ozonolysis}}$ $CH_3CH=CH-CH=CHCH_3$

2,4–Hexadiene

B42. (*d*) :

$CH_3-C(CH_3)(CH_3)-CH=CH_2 \xrightarrow{H^+} CH_3-C^+(CH_3)-CH-CH_3$

2°-Carbocation (less stable)

$\xrightarrow[\text{shift}]{1,\ 2\text{-methyl}}$ $CH_3-C^+(CH_3)-CH(CH_3)-CH_3$

3°-Carbocation (more stable)

$\downarrow -H^+$

$CH_3-C(CH_3)=C(CH_3)-CH_3$

2, 3-Dimethylbut-2-ene

B43. (*c*) :

(A) $\xrightarrow{HCl}$ 1-Chloro-1-methylcyclohexane

(B) $\xrightarrow{HCl}$ 1-Chloro-1-methyl cyclohexane

B44. (*d*) : Benzene + O_2 $\xrightarrow{V_2O_5}$ Maleic anhydride

B45. (*d*) :

No. of π bonds = 4

No. of π bond electrons = 4 × 2 = 8

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B46.(*d*) : The enthalpy of hydrogenation is inversely proportional to the stability of alkene
Correct order : III > II > I

B48. (*d*) : $HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$
Presence of $KHSO_4$ will decrease the concentration of NO_2^+ and hence reaction will be slower.

B49. (*c*): $HC \equiv CH \xrightarrow{NaNH_2, liq.NH_3} HC \equiv C^-:Na^+ \xrightarrow{CH_3CH_2Br}$ But-1-yne (x)

$NaNH_2$, liq.NH_3

$CH_3CH_2C \equiv CCH_2CH_3 \xleftarrow{CH_3CH_2Br} Na^+:C^- \equiv C-CH_2CH_3$
Hex-3-yne (Y)

B50.(*a*) : In biphenyl, all carbon atoms are sp^2 hybridised and hence all lie in same plane.

B53.(*a*) : Correct order of acidic strength is:

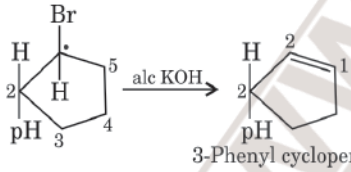
$H-C\equiv CH$ (two acidic hydrogens) > $CH_3-C\equiv CH$ (one acidic hydrogen) > $CH_2=CH_2$ > CH_3-CH_3

B54.(*c*) : There is no change in bond angles and bond lengths in the conformations of ethane. There is only change in dihedral angle.

B55.(*d*) : $CH_3-C\equiv CH \xrightarrow[H_2SO_4]{H_2O, Hg^{2+}} CH_3-\underset{OH}{\underset{|}{C}}=CH_2$ (A)

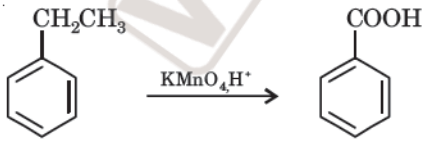
$\xrightarrow{\text{tautomerism}} CH_3-\underset{O}{\overset{\|}{C}}-CH_3$ (B)

B56.(*b*) : $\overset{sp^2}{CH_2}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv\overset{sp}{CH}$

B57.(*c*) : 

3-Phenyl cyclopentene

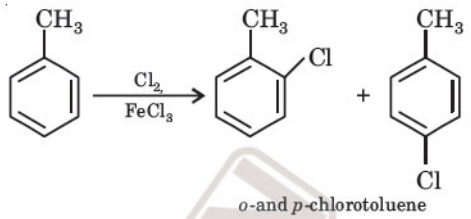
It is anti-elimination reaction in which H—atom from second carbon atom cannot be eliminated because it is in syn position. But H atom from 5th carbon gets eliminated.

B59.(*b*) : 

Benzoic acid

B60.(*d*) : $CH_3-C\equiv CH \xrightarrow{HBr} CH_3-\underset{Br}{\underset{|}{C}}=CH_2$

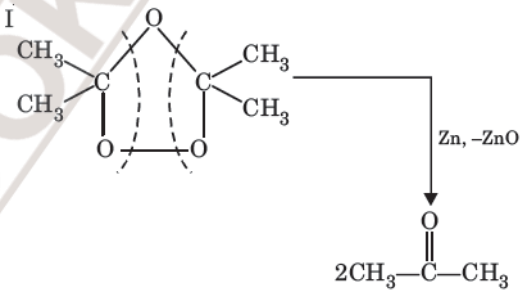
$\xrightarrow{HBr} CH_3-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3$
2,2-Dibromopropane

B61.(*b*) : 

o-and *p*-chlorotoluene

B62.(*c*) : $-NO_2$ group shows —R effect and withdraws electron density from the benzene ring and hence deactivates the ring towards electrophilic aromatic substitution.

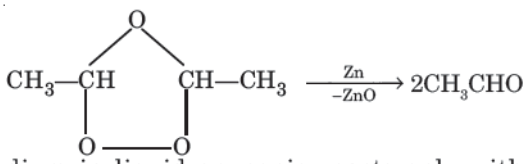
B63.(*a*): $CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3 \xrightarrow{O_3}$
2,3-Dimethylbut-1-ene



Acetone

B64.(*c*) : In all other structures, electron withdrawing $-NO_2$ group is present which intensifies the positive charge and destabilises the structures.

B65.(*a*) : $CH_3-CH=CHCH_3 \xrightarrow{O_3}$



B66.(*c*) : Sodium in liquid ammonia reacts only with terminal alkynes.

B67.(*a*) : $CH_3C\equiv CH + CH_3MgX \xrightarrow{\text{Dry ether}} CH_3C\equiv CMgX + CH_4$

B68. (*c*) : $\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv\overset{sp}{C}-\overset{sp^2}{\overset{+}{C}}H_2$

B69. (*b*) :

$\begin{matrix}CH_2COONa\\|\\CH_2COONa\end{matrix} + 2H_2O \longrightarrow \begin{matrix}CH_2\\\|\\CH_2\end{matrix} + 2CO_2 + 2NaOH$
Sodium succinate

B72. (*d*) : $C_6H_5CH_2-CH=CH_2 + HBr \xrightarrow{\text{peroxide}}$

$C_6H_5CH_2CH_2CH_2Br$
1–Bromo–3–phenylpropane

B73. (*b*) : Vinyl group on ozonolysis gives formaldehyde as one of the products.

B75. (*a*) : $\overset{5}{CH_3}-\underset{OH}{\overset{4}{CH}}-\overset{3}{CH_2}-\underset{O}{\overset{2}{C}}-\overset{1}{CH_3}$
4-Hydroxypentan-2-one

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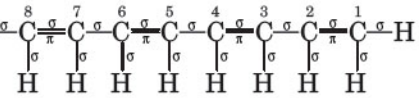
Competition File

B76. (*b*) : 

octa-1,3,5,7-tetraene

σ-bonds = 17, π bonds = 4

B77. (*e*) : $CH_3—CH_2—CH_2—CH_2—CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr}$

Hex-1-ene

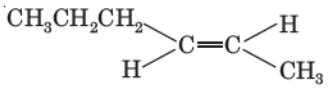
$CH_3CH_2CH_2CH_2CH_2Br$

1-Bromohexane

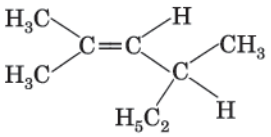
It is according to anti-Markovnikov rule.

B78. (*a*) : $CH_3CH_2CH_2C \equiv CCH_3 \xrightarrow[\text{Birch reduction}]{Li/NH_3}$

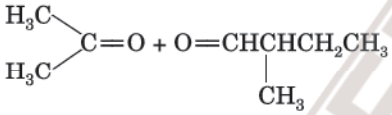
Hex-2-yne

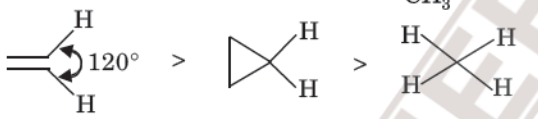


trans- hex-2-ene

B79. (*b*) :  $\xrightarrow[(ii)\ Zn,\ H_2O]{(i)\ O_3}$

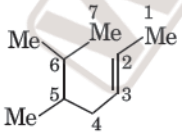
Optically active compound



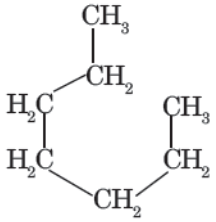
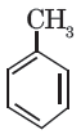
B80. (*b*) : 

sp^2	sp^3	sp^3
Trigonal planar	Tetrahedral	Tetrahedral
(II)	(I)	(III)

The bond angle in (II) is largest because 'C' is sp^2 hybridised. Therefore, bond angle is about 120. In both (I) and (III), carbon is sp^3 hybridised. However, the bond angle in (I) is larger than (III) because (I) contains a three membered cyclic ring, which is under a high angle strain. Due to this, the hydrogens in (I) are predisposed far away from each other, making the bond angle larger. Thus correct order of bond angle is II > I > III.

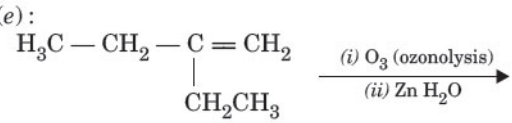
B81. (*a*) : 

5, 6-Dimethylhept-2-ene

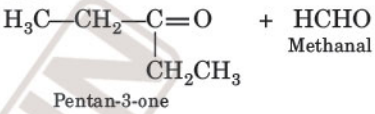
B82. (*a*) :  $\xrightarrow[10\text{-}12\ atm]{V_2O_5,\ 500^\circ C}$ 

n-Heptane

Toluene

B83. (*e*) : 

2-Ethylbut-1-ene

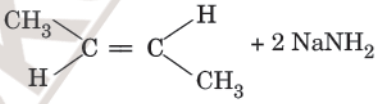


Pentan-3-one

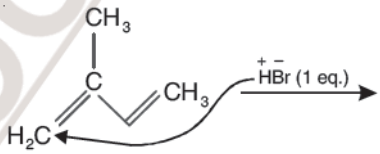
Methanal

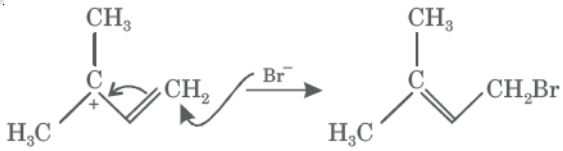
B84. (*b*) : $CH_3 — C \equiv C — CH_3 + 2\ Na \xrightarrow{liq.NH_3}$

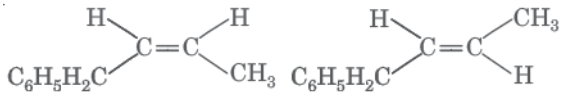
But-2-yne



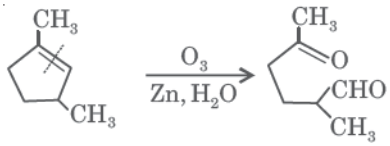
trans-but-2-ene

B85. (*b*) : 



B86. (*c*) : 

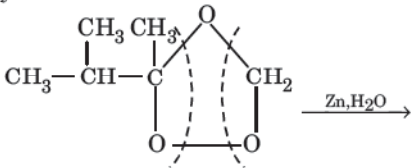
cis-form *trans*-form

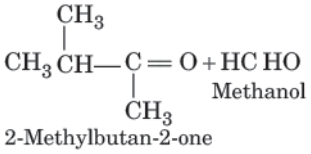
B87. (*d*) : 

5-keto-2-methylhexanal

B88. (*b*): $CH_3—\underset{CH_3}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{C}} = CH_2 \xrightarrow{O_3}$

2,3-Dimethylbut-1-ene





Methanol

2-Methylbutan-2-one

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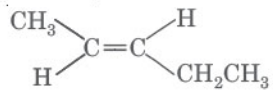
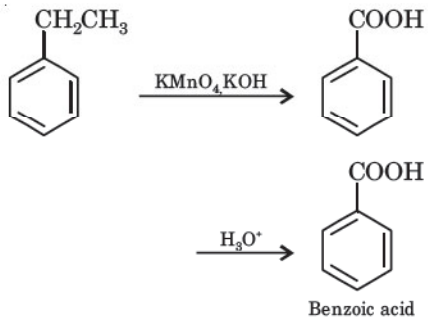
B89. (*b*): $CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-CH_3$

$\xrightarrow[\text{Dehydrohalogenation}\\-2\,HBr]{NaNH_2} CH_3-C\equiv C-CH_2-CH_2-CH_3$

$\downarrow$ Na, liq.NH_3, Birch reduction



B90. (*e*):



Benzoic acid

B91. (*b*): $CH_3CH=CH_2 + \overset{\delta-}{HO}\overset{\delta+}{Cl} \longrightarrow CH_3\overset{+}{C}HCH_2Cl$ (Intermediate)

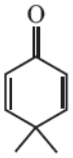
$\xrightarrow{OH^-} CH_3\underset{\underset{OH}{|}}{C}HCH_2Cl$

B92.(*d*) : On heating with alcoholic KOH or $NaNH_2$ in an inert solvent, the triple bond of but-1-yne gets shifted to but-2-yne.

$\underset{\text{But-1-yne}}{CH_3CH_2-C\equiv CH} \xrightarrow[\Delta]{alc.KOH} \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH}$

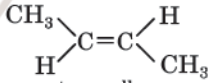
B93.(*b*) : $CH_3-CH=CH_2 + B\dot{r} \longrightarrow CH_3-\dot{C}H-CH_2Br$

B94.(*b*) :



is non-aromatic and is least resonance stabilized.

B95.(*c*) : $CH_3-C\equiv C-CH_3 \xrightarrow{Na/liq.NH_3}$

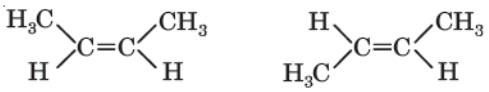


trans-alkene

B96.(*c*) : $CH_3-\underset{\underset{Cl}{|}}{\overset{Cl}{\overset{|}{CH}}} \xrightarrow[-HCl]{alc.\ KOH} CH_2=CH-Cl$ Vinyl chloride

$\xrightarrow[-HCl]{alc.\ KOH} CH\equiv CH$ Ethyne

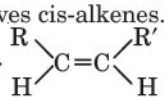
B97.(*a*) :



cis But-2-ene exhibit geometrical isomers trans

B98. (*b*): Catalytic reduction of alkynes with hydrogen in the presence of Pd/C gives cis-alkenes.

$R-C\equiv C-R' + H_2 \xrightarrow{Pd/C}$



cis – but-2-ene

B99. (*c*): $CH_3CH_2CH_2CH_2CH_2CH_3$ (Hexane)

$CH_3-\underset{\underset{CH_3}{|}}{CH}CH_2CH_2CH_3$ (2-Methylpentane)

$CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}CH_2CH_3$ (3-Methylpentane)

$CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3$ (2,2-Dimethylbutane)

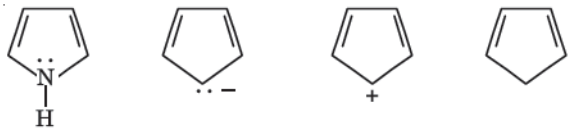
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ (2,3-Dimethylbutane)

B100. (*a*): $C_6H_5-C\equiv CH \xrightarrow[H_2SO_4]{H_2O,\,HgSO_4} C_6H_5-\underset{\underset{OH}{|}}{C}=CH_2$

Phenyl acetylene

$\xrightleftharpoons{\text{tautomerises}} C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$ Acetophenone

B101. (*a*): According to Huckel rule, the compounds having $(4n + 2)\pi$ electrons are aromatic.



6 π e⁻ (A) 6 π e⁻ (B) 4 π e⁻ (C) 4 π e⁻ (D)

B102. (*d*) : $CH_3-C\equiv\overset{-}{\overset{+}{C}}H + \overset{-}{C}H_3\overset{+}{M}gBr \longrightarrow$

$CH_3-C\equiv\overset{-}{C}\,\overset{+}{M}gBr + CH_4$

B104.(*a*) : $CH_3CH_2\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2} \xrightarrow{alc.KOH} CH_3CH_2\underset{\underset{Br}{|}}{C}=CH_2$

$\xrightarrow[liq.NH_3]{NaNH_2} CH_3CH_2C\equiv CH$

B105.(*c*) : $NOCl \rightleftharpoons NO^+ + Cl^-$

$CH_3-CH=CH_2 + NO-Cl \longrightarrow$

$CH_3-\overset{+}{C}H-CH_2\,NO$

$CH_3\overset{+}{C}H-CH_2NO + Cl^- \longrightarrow CH_3\underset{\underset{Cl}{|}}{C}H-CH_2NO$

B106.(*b*) : The conversion is carried out first by treating with alc. KOH followed by $NaNH_2$.

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B107. (*d*) : $CH_3CH_2C \equiv CH \xrightarrow{NaNH_2} CH_3CH_2C \equiv CNa^+$

$CH_3CH_2CH_2CH_2Br + Na^+C \equiv CCH_2CH_3$

$\longrightarrow CH_3CH_2CH_2CH_2C \equiv C - CH_2CH_3$

3-Octyne

B108. (*b*) : $\overset{sp^2}{CH_2} = \overset{sp^2}{C} = \overset{sp^2}{CH_2}$

C. *mcq with more than one correct answer*

C2. (*a,c*) : $HC \equiv C-CH_2-CH_3 + H_2O \xrightarrow{Hg^{2+},H^+}$

But–1–yne

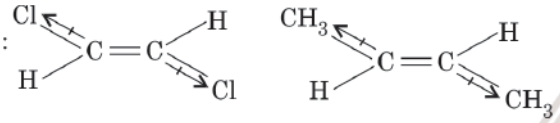
$CH_2 = C(OH)-CH_2CH_3 \longrightarrow CH_3-C(=O)-CH_2CH_3$

$CH_3-C \equiv C-CH_3 + H_2O \xrightarrow{Hg^{2+},H^+}$

But–2–yne

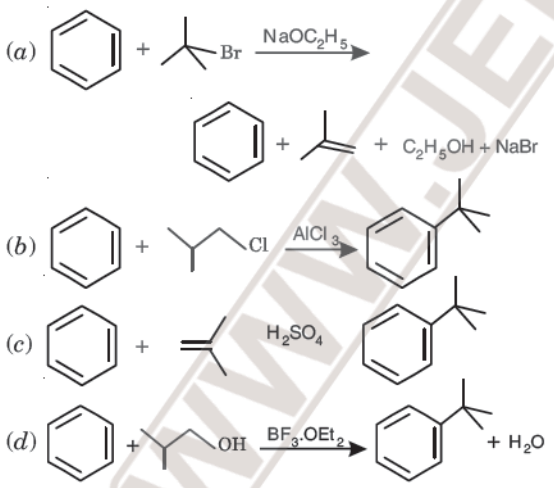
$CH_3-CH = C(OH)-CH_3 \longrightarrow CH_3CH_2-C(=O)-CH_3$

C8. (*a,d*) :



C14. (*b,c*) : (*b*) and (*c*) are anti-aromatic and unstable. (*a*) is non-aromatic and (*d*) is aromatic and are stable at room temperature.

C15. (*b,c,d*) :



D. *mcq based on comprehension*

D1. (*b*) : $CH_3-CH=CH-CH_3 \xrightarrow[KMnO_4]{\text{cold alk}}$

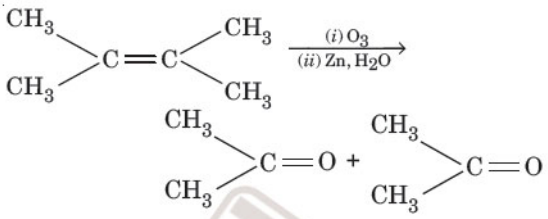
$CH_3-CH(OH)-CH(OH)-CH_3$

Butane-2, 3- diol

D2. (*b*) : $CH_3-CH=CH-CH_3 + 4\,(O) \xrightarrow[KOH]{KMnO_4}$

$CH_3COOH + CH_3COOH$

D3. (*a*) :



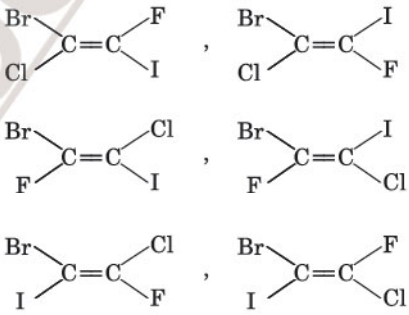
D4. (*b*) : $CH_3-C(CH_3)=CH_2 + 4[O] \xrightarrow{\text{alk } KMnO_4} CH_3-C(CH_3)=O + HCOOH$

$HCOOH \xrightarrow{[O]} CO_2, H_2O$

Integer Type Questions

1. (3) : *trans*-but-2-ene, *trans*-1,2-dichloroethene, but-2-yne

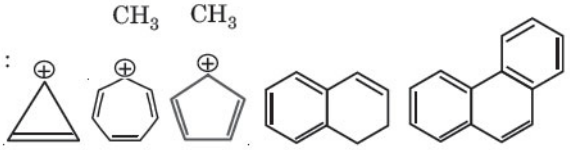
2. (6) : Six isomers :



3. (4) : 2-Methylbut-2-ene, but-2-ene, propene, pent-2-ene

4. (2) : $CH_3-\overset{3^\circ}{CH}(CH_3)-\overset{3^\circ}{CH}(CH_3)-CH_3$

5. (5) :



NCERT Exemplar Problems : MCQs Type-I

1. (*d*) : Boiling point decreases with increase in branching and with decrease in total number of carbon atoms. Thus, the correct order is

C (*n*-pentane) > B (2-methylbutane) > D (2, 2-dimethylpropane) > A (*n*-butane).

2. (*a*) : Reactivity decreases down the group.

5. (*a*) : $\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} \xrightarrow[\text{Markovnikov rule}]{HBr} \underset{\substack{\text{1(major product)}\\ + CH_3CH_2CH_2CH_2Br\\ \text{C (minor product)}}}{CH_3CH_2\underset{Br}{CH}-CH_3}$

Since I contains a chiral carbon, it exists in two enantiomers which are mirror images of each other.

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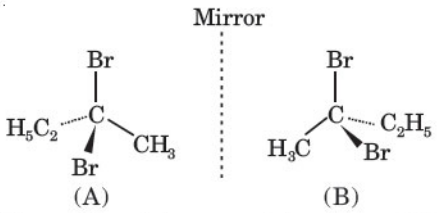
Competition File



Thus, the mixture consists of A and B as major and C as minor product.

8. (*b*) : *sp*-hybridised carbon is more electronegative than a sp^3 hybridised carbon and hence can accommodate the negative charge better. Therefore, B is more stable than C. Since $-CH_3$ group has + I effect, it intensifies the negative charge and therefore, destabilises A as compared to B. Thus, the order of stability is : B > A > C.

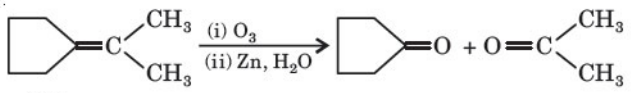
9. (*d*) : The larger the number of alkyl groups attached to the double bonded carbon atoms, the more stable is the alkene and more reactive is the corresponding alkyl halide. So correct order is : A > C > B.

NCERT Exemplar Problems : MCQs Type-II

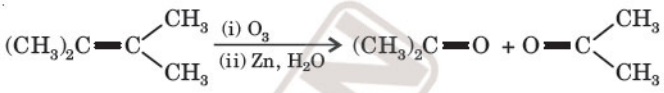
11. (*c,d*) : In which CH_4 does not undergo complete combustion to give CO_2 and H_2O.

12. (*c,d*) : The alkenes which have two substituents on each carbon atom of the double bond give mixture of ketones on ozonolysis, i.e., (*c*) and (*d*).

(*c*) :



(*d*) :



13. (*c,d*) : 1-methylpropyl and 1-methyl ethyl are IUPAC names of sec-butyl and isopropyl groups. But both these names are recommended by IUPAC.

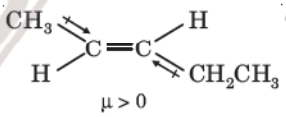
14. (*a,d*) : Both 2′, 2′ -dimethyl propyl and neopentyl groups are recommended names by IUPAC.

18. (*a,c*) : Cyclopropenyl cation (2π electrons) and diphenyl (two benzene rings have 6 π electrons each) are aromatic.

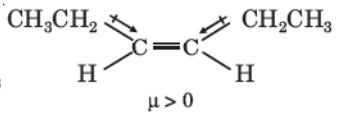
(*b*) : Cyclooctatetraene is not planar and has 8 π electrons.

(*d*) : Cyclopropenyl anion has 4π electrons. Therefore, (*b*) and (*d*) are not aromatic.

19. (*b,c*) :



trans-Pent-2-ene



cis-Hex-3-ene

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Unit Practice Test

for Board Examination

Time Allowed: 1 Hr. ***Maximum Marks: 25***

1. Complete the reaction : (1)

$CH_3CH_2COOH + HI \longrightarrow$

2. Which of the following has the highest boiling point ?

2-Methylpentane or 2,2-dimethylbutane (1)

3. Write the IUPAC name of (1)

4. Will the compound $CH_3—CH=CCl(CH_3)$ show geometrical isomerism ? (1)

5. Which of the two : cyclopentadienyl anion or cyclopentadienyl cation is not aromatic ? (1)

6. Give two chemical tests to distinguish 1-pentene from *n*-pentane. (2)

7. Write structural formulas and IUPAC names of all possible isomers having molecular formula C_5H_8 and one triple bond. (2)

8. Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Explain with one example. (2)

9. Addition of HBr to $CH_2=CH—CH_3$ gives 2-bromopropane while in the presence of benzoyl peroxide, the same reaction gives 1-bromopropane. Explain and give mechanism. (3)

10. Complete the following reactions :

(*i*) $C_6H_6 + CH_3Cl$, anhyd. $AlCl_3 \longrightarrow$

(*ii*) $CH_3C\equiv CCH_3 \xrightarrow[(ii)\ Zn,\ H_2O]{(i)\ O_3}$

(*ii*) $CH_3CH_2C\equiv CH \xrightarrow[Heat]{\text{acidic } KMnO_4}$ (3)

11. What is meant by electrophilic substitution reaction? Explain the mechanism of nitration of benzene. (3)

12. (*a*) How will you convert benzene to following :

(*i*) *m*-nitrochlorobenzene

(*ii*) acetophenone

(*iii*) *p*-nitrotoluene

(*b*) Why is benzene extra ordinarily stable though it contains three double bonds? (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part II of the book.

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UNIT 14

ENVIRONMENTAL POLLUTION

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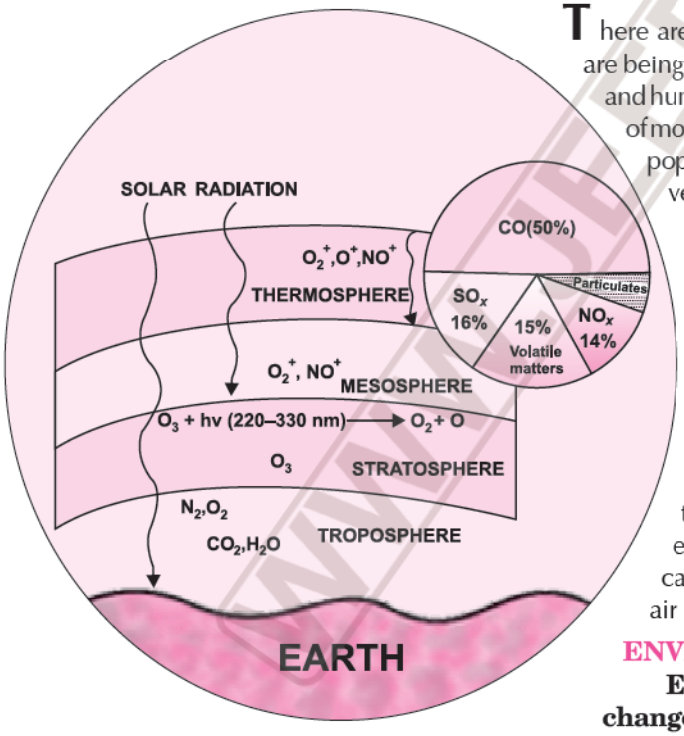

There are a number of substances (toxic as well as non-toxic) which are being added to our surroundings or environment by natural events and human activities. These are in fact, the undesirable consequences of modern civilization, increased use of natural resources, increasing population, advancement in industries, increase in number of vehicles, etc. These substances which are continuously going into air, water and soil bring about undesirable changes in physical, chemical and biological characteristics of our environment and adversely affect the life processes of animals and plants.

The branch of science which deals with the chemical phenomena occurring in the environment is called **environmental science.**

This deals with the study of the origin, transport, reactions, effects and consequences of chemical species in the environment. The contamination of any part of the environment is called pollution and the substances which cause pollution are called pollutants. The pollutants can cause air pollution, water pollution or soil pollution.

ENVIRONMENTAL POLLUTION

Environmental pollution is the **effect of undesirable changes in our surroundings (air, water or land) that have harmful effects on human, animal and plant life as well as on materials.** Pollution may be natural or man made. It can be classified according to the components of environment being damaged. These are :

(*i*) Air pollution
(*ii*) Water pollution
(*iii*) Soil (land) pollution.

A substance which causes pollution is called **pollutant.** The pollutants can be solid, liquid or gaseous substances. These can be *degradable* like discarded vegetables and fruits which rapidly break down by natural

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processes. The pollutants can also be *non-degradable* such as aluminium pieces, mercury, DDT etc. which remain in the environment in an unchanged form for many decades. In general,

pollutants are the substances made by us, used by us and even thrown by us as waste products which pollute the environment directly or indirectly in one way or other.

Do you know that an average human being needs about 12–15 times more air than the food. So, even a small amount of pollutants in the air become significant compared to similar levels present in the food.

Can you believe, man is the principal source of pollution ?

SOME COMMONLY USED TERMS

Some commonly used terms in environmental chemistry are :

1. Pollutant

***When the concentration of a substance already present in nature or of a new substance increases to undesirable proportions causing danger to human beings, other animals or vegetation and other materials, the substance is treated as a* pollutant.** The pollutants spoil the environment and are harmful to living organisms and other materials . The common pollutants are :

(*i*) gases like carbon monoxide, sulphur dioxide, oxides of nitrogen, etc.
(*ii*) compounds of metals like lead, mercury, zinc, cadmium, arsenic, etc.
(*iii*) pollen grains, dust
(*iv*) pesticides and detergents
(*v*) sewage and
(*vi*) radioactive substances.

It may be noted that normally highly toxic substances are considered as pollutants. However, the substances which are normally harmless can cause pollution if they are present in undesirable concentrations. For example, nitrate is added to soil as a fertilizer to increase growth of the plants, but an excessive concentration of nitrate present in drinking water can be harmful especially to young children.

2. Contaminant

***A substance which does not occur in nature but is introduced by human activity into the atmosphere affecting its composition* is called contaminant.** It may or may not be harmful to the living organisms or non-living components.

The contaminant is classified as pollutant when it has some harmful effect. For example, pyrosulphuric acid ($H_2S_2O_7$) leaked from a defective tank killed many persons and caused skin and breathing problems to many persons in Delhi. Since pyrosulphuric acid does not occur in the atmosphere, so it is a contaminant. But because of its dangerous effect, it is also regarded as a pollutant.

Generally, highly toxic substances are considered as pollutants.

3. Source

***The site from which the pollutants or contaminants come* is called source.** Every pollutant originates from a source. The source is particularly important because its knowledge helps to develop the methods to eliminate pollutants.

4. Sink

***The material or medium which consumes or interacts with a long lived pollutant* is called sink.** For example, a marble wall acts as a sink for atmospheric sulphuric acid because of the reaction :

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

The oceans are sinks for atmospheric carbon dioxide and other water soluble gases.

Ground water and subsoil water also act as sinks for pesticides used in agriculture.

5. Receptor

***Anything that is affected by the pollutants* is called receptor.** For example, human beings are the receptor of photochemical smog causing irritation in eyes and breathing problems.

6. Speciation

Speciation means the identification of different chemical forms or species of an element or a compound present in the environment. For example, mercury may be present in the environment in various forms such as elemental mercury, mercury salts, organometallic mercury species; CH_3Hg^+, $(CH_3)_2Hg$. It is very essential to identify the chemical species of the pollutants because some species may be more toxic than others and need special care. For example, alkyl mercury derivatives [CH_3Hg^+,$(CH_3)_2$ Hg] are highly poisonous as compared to other species of mercury.

7. Threshold Limit Value (TLV)

This indicates the permissible limit of a pollutant toxic in atmosphere to which a healthy worker is exposed during 8 hours a day or 40 hours a week for life time without any adverse effects. TLVs are determined by experimentation on animals, medical knowledge and experience, epidemiology surveys and environmental studies.

For example, TLV of CO is 50 ppm and that of CO_2 is 5000 ppm. But TLV for a poisonous gas phosgene is only 0.1 ppm.

In an environment pollution process, a pollutant originates from a **source.** It is transported by air or water or is dumped on land by man. Some of the pollutants may be absorbed (assimilated) or chemically changed by the **sink.** The remaining pollutants build up to harmful concentrations and affect the **receptor.** This is shown in Fig. 1.

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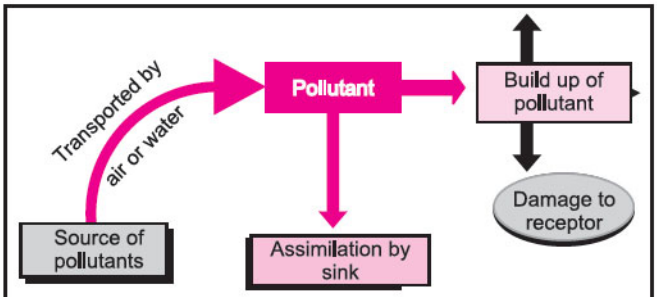

Fig. 1. A schematic representation of an environmental pollution process.

CHEMICAL REACTIONS IN ATMOSPHERE

The gaseous envelope surrounding the earth is known as **atmosphere.** The two major components of dry and clean air in the atmosphere (by volume) are nitrogen (78.09%) and oxygen (20.95%). Argon (0.934%) and carbon dioxide (0.034%) are the minor components of the atmosphere. Air can hold water vapour from 0.1 to 5% by volume and also contains trace of elements such as noble gases (neon, helium, krypton, xenon), hydrogen, methane, sulphur dioxide, ammonia, ozone, etc.

The atmosphere surrounding us may be divided into four regions :

(i) troposphere
(ii) stratosphere
(iii) mesosphere
(iv) thermosphere.

About 80% of the total mass of air and almost all of the water vapours of the atmosphere is found in the inner layer known as **troposphere** which extends to 8 to 12 km above the earth's surface. This is the most important region of the atmosphere because it is the domain of all living organisms including animals and plants. This has homogeneous composition of major gases (N_2, O_2, CO_2, water-vapour and noble gases). It has decreasing temperature with increasing altitude from the earth surface with a minimum around –56°C at the maximum height of the troposphere. However, on certain occasions, the temperature may increase to some extent with altitude instead of decreasing. Such a situation is called **temperature inversion** and is due to trapping of a layer of cold air by a warmer upper layer.

With increasing altitudes from the earth's surface, the other regions are *stratosphere* (11– 50 km), *mesosphere* (50 – 90 km) and *thermosphere* (90 – 500 km). The stratosphere contains nitrogen, oxygen and ozone.

In **stratosphere,** the temperature rises with increasing altitude showing a maximum of –2°C. This phenomenon is due to the presence of ozone which may absorb ultraviolet radiation and raises the temperature in this region. This act of ozone protects us from the harmful effects of sun's ultraviolet radiation. This region contains N_2, O_2, O_3 and O-atoms. Due to the presence of ozone layer, this layer is also called **ozonosphere.**

The region beyond stratosphere is dominated by positive ions such as O_2^+, O^+ and NO_2^+ in addition to N_2 and O_2 and is called **mesosphere.** This extends upto 90 km.

Above 90 km, the region is called **thermosphere** which contains ions such as O_2^+, O^+, NO^+ and free electrons.

The regions mesosphere and thermosphere are collectively called **ionosphere** because these contain ionized gases.

The different regions of the atmosphere are shown in Fig.2.

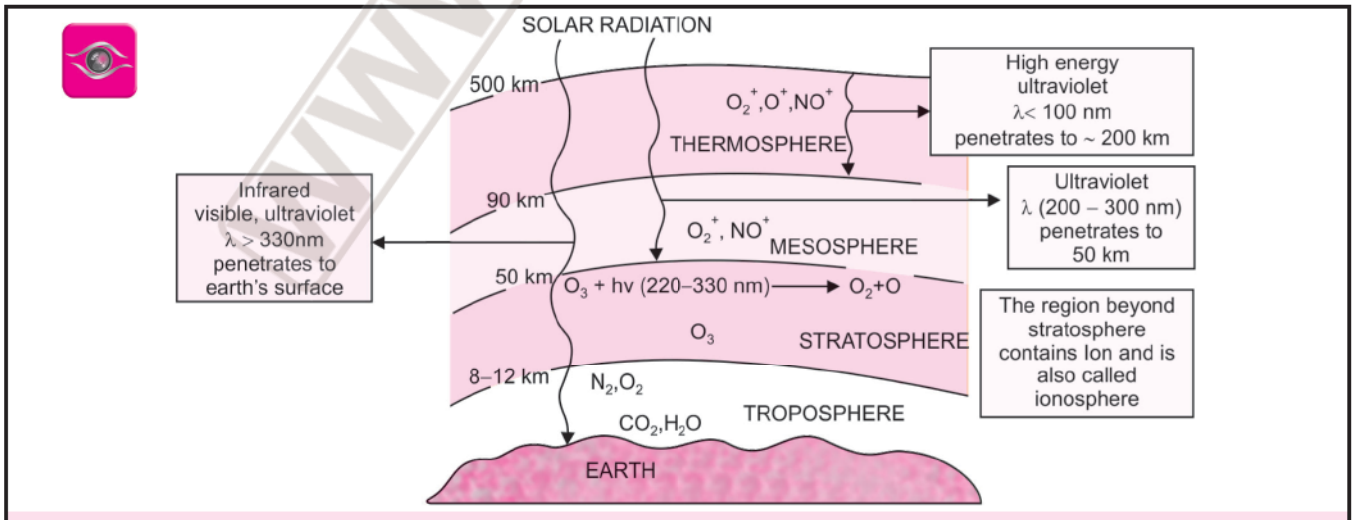

Fig. 2. Major regions of atmosphere.

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TYPES OF ENVIRONMENTAL POLLUTION

The environmental pollution may be of the following types :

1. Atmospheric pollution

2. Water pollution

3. Soil or land pollution.

The atmospheric pollution is generally studied under two heads :

(*a*) Tropospheric pollution

(*b*) Stratospheric pollution.

Tropospheric pollution is much more widespread and we all are concerned about it. Since only a few substances produced by human activity reach the stratosphere, its pollution results in the depletion of ozone layer, which may result into very serious problems.

AIR POLLUTION

Air is never found clean due to natural and man-made pollution. Gases such as carbon monoxide, nitrogen oxides, sulphur oxides, hydrogen sulphide and many volatile organic compounds are continuously released into the atmosphere due to natural and human activities. ***Air pollution occurs when the concentration of a normal component of the air or a new chemical substance added or formed in air builds up to undesirable proportions causing harms to humans, other animals, vegetation and materials.***

The chemical substance causing pollution is called **air pollutant.** About 90% of air pollution problems are caused by the pollutants such as carbon monoxide, sulphur oxides, volatile organic compounds, nitrogen oxides and suspended particulate matter (such as carbon, dust, pollen, metal, etc.) as shown in Fig. 3.

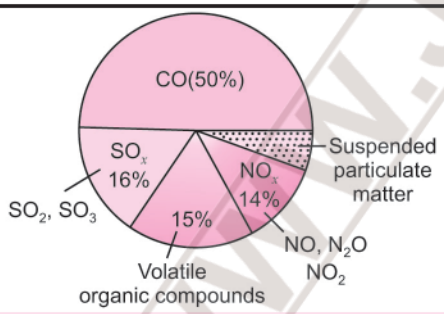

Fig. 3. Major air pollutants (approximate bundance).

Sources of Air Pollutants

The air pollution is caused by natural activity and human activity. The natural sources of air pollution are volcanic eruptions, forest fires (caused by lightning), pollen dispersal, evaporation of volatile organic compounds from leaves, bacterial decomposition of organic matter, wind erosion of soil and natural radioactivity.

The main human activities responsible for polluting the air are burning of fuels (coal, oil, gasoline, etc.) in power and industrial plants and in motor vehicles and industrial processes and industrial wastes.

Air Pollutants

There are two types of air pollutants :

1. *Primary air pollutants*

2. *Secondary air pollutants.*

1. Primary air pollutants

A primary air pollutant is a harmful chemical substance that directly enters the air as a result of natural events or human activities. The primary pollutants are :

(*i*) Carbon oxides (CO and CO_2)

(*ii*) Nitrogen oxides (NO)

(*iii*) Sulphur oxides (SO_2)

(*iv*) Hydrocarbons

(*v*) Suspended particulate matter.

2. Secondary air pollutants

A secondary air pollutant is a harmful chemical that forms in the air due to a chemical reaction between two or more air components or a primary pollutant and one or more air components. For example, sulphur dioxide is a primary pollutant in air. It reacts with oxygen gas in the atmosphere to form the secondary pollutant sulphur trioxide (SO_3).

$$\underset{\text{Primary pollutant}}{2SO_2} + O_2 \longrightarrow \underset{\text{Secondary pollutant}}{2SO_3}$$

Even, the sulphur trioxide formed may react with the water vapour in air to form sulphuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Sulphuric acid is, therefore, also a secondary pollutant.

The common secondary pollutants are :

SO_3, H_2SO_4, NO_2, N_2O, HNO_3, H_2O_2, O_3, nitrate and sulphate salts, etc.

Pollutants can also be classified as:

(*i*) Biodegradable pollutants and

(*ii*) Non-biodegradable pollutants

(*i*) **Biodegradable pollutants.** *These are the materials which are easily decomposed by the microorganisms either by the nature itself or by suitable treatment so that their degraded products donot cause any serious effects on the environment.* For example, domestic sewage, cow-dung etc.

(*ii*) **Non-biodegradable pollutants.** *These are the materials which donot undergo degradation or degrade slowly or partially and their presence even in very small amounts in the environment is very harmful for humans as well as plants life.* These pollutants not only accumulate in the environment but are often biologically magnified because they move in biochemical cycles and along food chains. For example, aluminium, mercury, D.D.T., plastic materials, many chemicals, nuclear wastes etc.

The main air pollutants and their major sources are given in Table 1.

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Table 1. Some common air pollutants and their major sources.

Pollutant	Major pollutant source
CO	Transportation, autoexhaust, petroleum, paper industries, iron and steel industries, solid waste disposals.
CO_2*	Fuel combustion and industrial processes.
SO_2	Metallurgical operations, combustion of coal and oil, paper, manufacture of H_2SO_4.
NO, NO_2	Fertilizer industries, explosive industries, manufacture of HNO_3.
H_2S	Petroleum refining, coke ovens, natural gas plants.
Cl_2	Industrial processes such as paper, plastics, dyes, chlorinated hydrocarbons.
NH_3	Natural biological processes, industrial processes, ammonia works.
Hydrocarbons	Petroleum refineries, chemical processes, rubber manufacture, transportation, solid waste disposal.
Particulates	Volcanic eruptions, metallurgical operations such as smelting and mixing, incomplete combustion in industrial processes.

*Usually CO_2 is not considered as pollutant.

Other air pollutants are metals like Be, Ba, Cd, Fe, Mn, Pb, Hg, Ni, Zn (from mining and metallurgy), non-metals such as As, P, Se (from combustion of industrial fuels, fertilizers) radioactive substances (from nuclear power plants).

Industrial accidents can also play havoc for the environment. For example, an industrial accident occurred in the Union Carbide factory on December 3, 1984 in Bhopal. It released a large scale of poisonous MIC (methyl isocyanate) and caused excessive damage to all forms of life.

TROPOSPHERIC POLLUTION

The tropospheric pollution occurs because of the presence of undesirable solid or gaseous particles in air. The pollutants may be broadly classified into two major types :

1. Gaseous air pollutants. These include oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.

2. Particulate pollutants. These are dust, fumes, mist, spray, smoke, etc.

These are briefly discussed.

SOME COMMON AIR POLLUTANTS

Although there are many sources of air pollutants, the common pollutants come from combustion processes. Let us discuss the major air pollutants.

A. GASEOUS AIR POLLUTANTS

1. Oxides of Carbon

(a) Carbon monoxide (CO)

It is one of the most serious air pollutant. It is a colourless, odourless and tasteless gas above 81 K. It is heavier than air and is not soluble in water. It is one of the most serious air pollutants. It is highly poisonous to living beings because of its ability to block the delivery of oxygen to the organs and the tissues.

Sources of CO in air

The **main sources** of air pollution of CO are the automobile engines and defective furnaces. Some of the sources of CO in air are :

(*i*) Incomplete combustion of carbon, fossil fuel or carbon containing compounds.

$$2C + O_2 \longrightarrow 2CO$$

For example, the complete combustion of butane requires 6.5 moles of O_2 per mole of butane. If only 6.0 moles of O_2 are present, then 1 mole of CO and 3 moles of CO_2 are formed.

$$C_4H_{10}\,(g) + \tfrac{13}{2}\,O_2\,(g) \longrightarrow 4CO_2\,(g) + 5H_2O\,(l)$$

$$C_4H_{10} + 6O_2\,(g) \longrightarrow 3CO_2\,(g) + CO(g) + 5H_2O\,(l)$$

(*ii*) Reaction of carbon dioxide and carbon containing compounds at high temperatures in industrial processes such as blast furnace.

$$CO_2 + C \longrightarrow 2CO$$

(*iii*) Dissociation of carbon dioxide at high temperatures :

$$2CO_2 \rightleftharpoons 2CO + O_2$$

Some natural processes such as volcanic activity, natural gas emission, electrical discharge during storms, marsh gas production, seed germination, etc. release some CO in the atmosphere.

The main contribution of CO in air pollution is from human activity. Of the total carbon monoxide content in atmosphere, **about 74% is contributed by automobile exhaust (motor vehicles, aircraft, rail, road).** About 16% is contributed by forest fires and agriculture burning (burning of forest debris, crop residues, weeds and other vegetation). Industrial processes mainly iron and steel industries, paper, petroleum industries contribute about 9.6% of CO in atmosphere.

Sinks of CO

Though human activities are releasing CO in atmosphere and it is expected to double its concentration in surrounding atmosphere every 5 years. However, the actual increase in CO in atmosphere is less because of some natural sinks.

(*i*) Soil is the major sink for CO. Some microorganisms in soil remove CO from the atmosphere.

(*ii*) Some of the species in atmosphere such as hydroxyl (HO) and perhydroxyl (HOO) radicals, atomic oxygen and ozone help in the oxidation of CO to CO_2 and consequently, remove it from the atmosphere.

Harmful effects of Carbon monoxide

1. Effects of CO on human health

Carbon monoxide is very toxic because it combines with haemoglobin in the blood preventing

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its function as an oxygen carrier. It is particularly dangerous because it is odourless and therefore, is not easily detected. Haemoglobin (Hb) in the blood combines with oxygen and forms oxyhaemoglobin by a reversible process :

$$Hb + O_2 \rightleftharpoons HbO_2$$

Oxyhaemoglobin formed in the lungs is carried to the different cells in the body and gives oxygen. However, carbon monoxide combines more readily than O_2 with haemoglobin of blood to form carboxy haemoglobin which is about 300 times more stable than the oxygen-haemoglobin complex. Therefore, when CO is enhaled along with air, it combines with haemoglobin to form a stable compound carboxy haemoglobin, (HbCO).

$$Hb + CO \longrightarrow HbCO$$

As a result, the amount of haemoglobin for transport of O_2 decreases and it reduces blood's capacity for carrying oxygen. When the concentration of carboxyhaemoglobin in blood reaches about 3–4 percent, the oxygen carrying capacity of blood is greatly reduced.

This deficiency of oxygen results into many harmful effects such as reduction in awareness and judgement, dizziness, weak eye sight, headache, nervousness and cardiovascular disorders.

At higher concentrations of CO, suffocation, loss of consciousness or even death after several hours may occur. This is the reason why pregnant women who have the habit of smoking are advised not to smoke as increased CO level in blood may induce premature birth of the baby, spontaneous abortions or deformed babies. It is so poisonous that within half an hour, 1300 ppm is fatal.

⇒ Because of harmful effects of carbon monoxide, *it is dangerous to sleep in a closed room with a coke fire burning inside on a cold winter night.* When coke burns in an insufficient supply of oxygen (due to closed room), a lot of carbon monoxide is produced. This can cause poisoning and may lead to death.

Effects of CO on Plants

Carbon monoxide has detrimental effects on plants when exposed for longer times. It inhibits the nitrogen fixing ability of bacteria. It also affects leaf drop, leaf curling, decrease in leaf size and premature ageing of the plants.

Control of CO

The major sources of CO air pollution are human activities. The internal combustion engine is the primary source of CO emission. The exhaust of internal combustion engine consists of a mixture of CO, oxides of nitrogen (NO_x), hydrocarbons (H_c) and particulate matter. The variation of fuel-air ratios has significant effect on the constituents of exhaust gases. It has been observed that as the air-fuel ratio increases (leaner in fuel), the concentration of CO decreases. Therefore, CO-emissions may be lowered by using a cleaner air-fuel mixture. For example, when air-fuel ratio (wt./wt.) is more than about 16 : 1 in internal combustion engines, they emit virtually no CO.

Some of the **important attempts** which have been made for the control of CO pollution are given below :

(*i*) Internal combustion engines are modified to reduce the amount of pollutants formed during fuel combustion. The presence of excess air ensures complete combustion of CO and hydrocarbons to CO_2. Automobile carburettors are adjusted and cleaned regularly to the proper fuel-air ratios.

(*ii*) Some exhaust system reactors are developed which will complete the combustion process and decrease the amount of CO.

(*iii*) Catalytic converters can be fitted into exhaust pipes to cut down the CO emission. These anti-pollution catalysts eliminate the pollutants from exhaust gases before they are discharged into the atmosphere.

(*iv*) Substituted fuels for gasoline which will give low concentration of pollutants upon combustion are being tried. Natural gas in compressed form (CNG) and in liquefied form (LPG) has been used as a fuel. Though there are pollution free fuels, yet they are less economical and difficult to store and distribute.

(*v*) Attempts are being made to develop pollution free energy sources such as electric power, gas turbines, solar cells etc. However, these are less economical as compared to gasoline.

(*b*) Carbon dioxide (CO_2)

Carbon dioxide is a normal and essential component of the atmosphere. Animals exhale it. Therefore, it is vital to all forms of plant and animal life. It is normally not a pollutant. It is not an important contributor to acid rain. It can cause acidity when it dissolves in water, but it is relatively less soluble in water than the oxides of nitrogen and sulphur. Normally, it forms about 0.03% by volume of the atmosphere. However, human activities are changing the balance established by nature's carbon cycle. With the increased use of fossil fuels, a large amount of carbon dioxide gets released into the atmosphere. As a result, the concentration of CO_2 in the atmosphere is increasing to an alarming extent.

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Therefore, there is need to keep balance of CO_2 in the atmosphere.

Sources

The main sources of CO_2 in atmosphere are :

(*i*) Carbon dioxide is released into the air by respiration.

(*ii*) Incomplete combustion of fossil fuels and carbon containing compounds.

$$C + O_2 \longrightarrow CO_2$$

(*iii*) Many industrial processes also produce a lot of carbon dioxide. For example, decomposition of limestone during manufacture of cement releases lot of carbon dioxide into the atmosphere.

(*iv*) Carbon dioxide is also produced by biological decay of plants.

(*v*) Carbon dioxide gas is also emitted during volcanic eruptions.

Sinks of CO_2

The main sinks for CO_2 are natural processes. Ocean is an important sink of carbon dioxide. It contains most of the dissolved CO_2 in the form of carbonates, bicarbonates and organic compounds.

The carbon dioxide of the atmosphere is also removed from the atmosphere by photosynthesis process of plants. In a balanced ecosystem, the additionally released CO_2 in the atmosphere is regularly removed by green plants for the photosynthesis process and they in turn emit oxygen, thus maintaining the cycle.

Effects of CO_2

Normally carbon dioxide is harmless and is not a pollutant. However, the increasing concentration of CO_2 may affect the atmosphere, causing undesirable change in climate. This effect is known as **greenhouse effect** (discussed later).

Control of CO_2

The major sources of CO_2 are vehicles, plants and industries while the sinks are ocean and plants. The balance can be maintained by the following steps :

(*i*) The release of CO_2 from various industrial processes should be controlled.

(*ii*) The production of CO_2 from vehicles exhaust should be checked.

(*iii*) To adjust the balance of CO_2 in atmosphere, the main sink of CO_2 *i.e.*, forests should be developed.

2. Oxides of Nitrogen (NO_x)

A number of oxides of nitrogen (NO_x) such as nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), N_2O_3 (dinitrogen trioxide) and N_2O_5 (dinitrogen pentoxide) are entering the atmosphere due to natural sources and human activities. Out of these, only two oxides, NO and NO_2 are considered as pollutants.

Nitric oxide (NO) is colourless, odourless gas and nitrogen dioxide (NO_2) is reddish brown gas having pungent suffocating odour.

The irritant red haze in traffic and congested places is due to oxides of nitrogen.

Sources of NO_x

Dinitrogen and dioxygen are the main constituents of air. These gases donot react with each other at normal temperature. But at high altitudes when lightening strikes, they combine to form oxides of nitrogen.

The important sources of NO and NO_2 are given below :

(*i*) The two oxides of nitrogen NO and NO_2 come in atmosphere from the combustion at high temperature (above 1483K) in automobile engines and thermal generating stations. The basic reactions leading to the formation of these oxides of nitrogen are :

$$N_2(g) + O_2(g) \overset{1483K}{\rightleftharpoons} 2NO(g)$$

NO reacts instantly with oxygen to give nitrogen dioxide.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Rate of production of NO_2 is faster when nitric oxide reacts with ozone as in the stratosphere.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

(*ii*) Many industrial processes also release oxides of nitrogen in the atmosphere.

(*iii*) The natural sources of oxides of nitrogen are bacterial action in soil, forest fire and lightning.

Sinks of NO_x

Many natural processes acts as sink for oxides of nitrogen. These oxides are inherently unstable and decompose to N_2 and O_2 after some time. Therefore, the concentration of nitrogen oxides in the atmosphere tends to remain low. Some natural processes and photochemical reactions also take care of NO_x in the atmosphere and serve as sinks. The end product of these reactions is HNO_3. The probable mechanism for the change of NO_x to nitric acid are :

(*i*)
$$2NO + O_2 \longrightarrow 2NO_2$$
$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

(*ii*)
$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
$$NO_3 + NO_2 \longrightarrow N_2O_5$$
$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

The nitric acid acts as a temporary sink and it comes in the form of nitrate salts in acid rainfall or in dust.

Harmful effects of NO_x

The irritant red haze in the traffic and congested places is due to the oxides of nitrogen. The main harmful effects of oxides of nitrogen are :

1. NO is biologically less active and less toxic than NO_2 and therefore, does not have a significant adverse effect on human health even at high concentrations. However, it is oxidised by oxygen or

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ozone to nitrogen dioxide which is extremely toxic to living tissue. Like CO, NO binds to haemoglobin and decreases oxygen transport efficiency of blood.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

2. The oxides of nitrogen cause damage to the leaves of plants. Exposure of plants to NO_x causes leaf spotting and breakdown of plant tissues. Excessive concentration (10 ppm) of NO causes decrease in the rate of photosynthesis.

3. The sunlight reacts with nitrogen dioxide to produce highly active oxygen atoms.

$$NO_2 \xrightarrow{\text{Sunlight}} NO + O$$

The active oxygen attacks traces of hydrocarbons in the air and produces irritants which is called *photochemical smog*. This is a health hazard.

4. Acute exposure to NO_2 can also cause damage to human health. Nitrogen dioxide is a lung irritant and can lead to acute respiratory disease in children.

5. The nitrogen oxides are harmful to various textile fibres and metals. These also cause fading of dyes used in textiles.

Control of Nitrogen oxides

The important factors in the control of oxides of nitrogen are :

(*i*) NO in vehicular exhausts is converted into N_2 and traces of NH_3 with the help of some catalyst (platinum).

(*ii*) Nitrogen oxides in fuel gases can be removed by alkaline scrubbing solutions using $Ca(OH)_2$ and $Mg(OH)_2$.

(*iii*) The nitrogen oxides can also be removed by acidic scrubbing. This process also removes SO_2. This involves the following steps :

(*a*) The flue gases coming from power plants or industrial units contain NO, NO_2 and SO_2. These are introduced into an oxidizer in which the following reaction occurs :

$$NO_2 + SO_2 + H_2O \longrightarrow H_2SO_4 + NO$$

(*b*) The NO and NO_2 react to form N_2O_3 which is scrubbed by H_2SO_4 in a scrubber.

$$NO_2 + NO \longrightarrow N_2O_3$$

$$N_2O_3 + 2H_2SO_4 \longrightarrow 2NOHSO_4 + H_2O$$

The scrubbed flue gas is released to the atmosphere.

(*c*) The reaction product, $NOHSO_4$ is then decomposed in a separate chamber called decomposer and the resulting H_2SO_4 is recycled to the scrubber.

$$2NOHSO_4 + \frac{1}{2}O_2 + H_2O \longrightarrow 2H_2SO_4 + 2NO_2$$

(*d*) NO_2 is then converted to HNO_3 in a reactor.

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

Excess of NO and NO_2 is recycled into the oxidiser.

3. Oxides of Sulphur (SO_x)

Oxides of sulphur are probably the most harmful of the common gaseous pollutants. *Sulphur dioxide is the main pollutant among sulphur oxides.* It is a colourless gas with a pungent odour. It is generally accompanied by little of SO_3 obtained by partial oxidation of SO_2.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Under humid conditions, SO_3 reacts with water vapour to form H_2SO_4 droplets.

$$SO_3(g) + H_2O(l) \rightleftharpoons H_2SO_4(l)$$

Sources of Sulphur dioxide

Some of the important sources of sulphur dioxide in atmosphere are :

(*i*) Most of the sulphur dioxide in atmosphere originate through the combustion of fossil fuels which contain some sulphur.

(*ii*) The atmosphere contains H_2S by decay of organic matter. The H_2S gets readily converted into SO_2 by the following reaction :

$$H_2S + \frac{3}{2}O_2 \longrightarrow SO_2 + H_2O$$

(*iii*) Large amounts of SO_2 are added to the atmosphere during ore roasting processes of sulphur ores. For example, SO_2 is produced during roasting of metallic sulphide ores such as pyrites (FeS_2), copper glance (Cu_2S), galena (PbS), zinc blende (ZnS), etc.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

Zinc blende

$$3Cu_2S + 3O_2 \longrightarrow 6Cu + 3SO_2$$

Copper glance

(*iv*) Volcanic sources also contribute significantly to the SO_2 in atmosphere.

The combustion of any sulphur containing material results in the formation of SO_2 and SO_3. Sulphur dioxide is the major constituent (about 97%) of the mixture.

Sinks of SO_2

Sulphur dioxide in air can undergo several reactions and therefore, can be removed. A part of SO_2 combines with water droplets to form sulphurous acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

It can also be oxidised to sulphur trioxide in air but uncatalysed oxidation of sulphur dioxide is slow. But because the polluted air often contains particulate matter, it catalyses the oxidation of sulphur dioxide to sulphur trioxide.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

The reaction can also be promoted by ozone and hydrogen peroxide.

$$2SO_2 + O_3 \longrightarrow SO_3 + O_2$$

Sulphur trioxide combines with water vapour to form droplets of sulphuric acid.

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$$SO_3 + H_2O \longrightarrow \underset{\text{Aerosol droplet}}{H_2SO_4} \longrightarrow (H_2SO_4)_n$$

The sulphuric acid comes down in the form of acid rain and gives rise to a phenomenon known as acid rain (discussed later on).

Effects of SO_2

Sulphur dioxide and its compounds (formed from SO_2 such as SO_3, H_2SO_4 or sulphates) are dangerous air pollutants. These have dangerous effects on human life. Some of the harmful effects are :

1. SO_2 effects respiratory tract producing nose, eye and lung irritation. It has been reported that lower concentration of SO_2 causes respiratory diseases *e.g.*, asthama, bronchitis, emphysema in human beings. It also causes irritation to the eyes resulting in tears and redness. High concentration of SO_2 may cause lung diseases and lung cancer. SO_2 has been considered the most serious single air pollutant causing many health hazards.

2. Atmospheric SO_2 is also harmful for plants. It damages vegetable crops and affects plant growth and nutrient quality of plant products. The exposure of plants to SO_2 causes damage to leaf tissues and causes **chlorosis** (a bleaching or yellowing of normally green portions of the leaves). In areas, having high levels of SO_2 pollution, and formation of H_2SO_4, may damage the plants.

3. The marble and limestone, both forms of calcium carbonate ($CaCO_3$) are attacked by SO_2 and H_2SO_4. These react as :

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O$$

This causes deterioration of buildings, statues, etc.

4. The oxides of sulphur cause fading and deterioration of fabric, leather and paper.

5. They affect the colour of the paints.

Control of SO_2 pollution

The various methods to control SO_2 pollution are given below :

(*i*) A number of processes are being used to remove sulphur from fuels before combustion.

(*ii*) Sulphur dioxide may be removed from flue gases. It can be easily eliminated by using chemical scrubbers.

Some of the methods to remove SO_2 chemically from the flue gases are :

(*a*) The most widely used method is limestone treatment in which finely divided limestone is directly introduced to the boiler. In this method, heat calcines the limestone forming quick lime. Quicklime reacts with SO_2 in the flue gas forming calcium sulphate.

$$CaCO_3 \longrightarrow CaO + CO_2(g)$$

$$CaO + SO_2 + \frac{1}{2}O_2 \longrightarrow CaSO_4$$

Solid $CaSO_4$ is removed and disposed off. However, the method is economical but it poses a problem of waste disposal.

(*b*) Sulphur dioxide produced may be passed through a lime slurry. This process is known as lime slurry scrubbing.

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$

The waste ($CaSO_3$) from this method can be used to prepare *gypsum* by oxidation of $CaSO_3$.

$$CaSO_3 + \frac{1}{2}O_2 + 2H_2O \longrightarrow CaSO_4.\,2H_2O$$

(*c*) Sulphur dioxide may be removed by first treating with sodium hydroxide and then with calcium hydroxide as:

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$
$$Ca(OH)_2 + Na_2SO_3 \longrightarrow CaSO_3 + 2NaOH$$

In this method, the expensive sodium hydroxide solution is regenerated with inexpensive lime.

(*iii*) Alternative energy sources such as hydroelectric plants and nuclear power plants may be used in place of thermal power plants using burning of coal (containing sulphur). However, these are not economical.

4. Hydrocarbons

Many hydrocarbons of low molecular mass are gases or volatile liquids and are present in air at ordinary temperature. Among these, methane is the most abundant hydrocarbon pollutant.

Sources of hydrocarbons

(*i*) Hydrocarbons are formed by incomplete combustion of fuel used in automobiles.

(*ii*) Methane is released into the air in large quantities by the anaerobic decomposition of organic matter present in soil, water and sediments.

$$\underset{\text{Organic matter}}{2CH_2O} \xrightarrow{\text{bacteria}} CH_4 + CO_2$$

(*iii*) Evaporation of organic solvents such as benzene, toluene, etc. during industrial operations add to hydrocarbon pollution.

(*iv*) Some hydrocarbon pollution also takes place due to burning of fuels such as coal, wood, kerosene, etc.

(*v*) Some trees also emit large quantities of hydrocarbons into the air.

Effects of hydrocarbons

(*i*) Hydrocarbons are carcinogenic and therefore cause cancer.

(*ii*) They harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.

(*iii*) Due to their photochemical reactions with oxygen and oxides of nitrogen, they form photochemical oxidants and photochemical smog. This has very hazardous effect on the human being and plants.

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B. PARTICULATES IN AIR POLLUTION

1. Particulates

The small sized solid particles and *liquid droplets which range in size from* 2×10^{-10} *m (0.0002 μm) to* 5×10^{-4} *m are collectively* called as **particulates.** These particles are usually individually not visible to the naked eye. However, small particles often collectively form a haze that restricts the visibility. The particulate matter in the range 0.001 to 10 mm range is commonly visible as suspended in the air near the sources of pollution.

These particulates include carbon (soot), metals, metal salts, cement dust, fly ash, hydrocarbons, soil dust, pulverized coal, asbestos dust, mineral particles, etc.

The particulates in the atmosphere may be **viable** or **non-viable.** The **viable particulates** are the small living organisms which are dispersed in the atmosphere. These include bacteria, moulds, fungi, algae, etc. Some of these viable particulates cause allergic reactions on human beings. Fungi can also cause plant diseases.

Non-viable particulates are formed either by the breakdown of large materials or by the condensation of minute particles and droplets.

Types of Particulates and their Sources

There are four types of non-viable particulates in the atmosphere injected into the atmosphere through human activity.

1. Smoke

These are very small soot particles. These consist of solid or mixture of solid and liquid particles formed during combustion of organic matter. Oil smoke, tobacco smoke and carbon smoke from burning fossil fuels, garbage and dry leaves are typical examples of this type of particulate materials. Their common sources are :

(*i*) Carbon particles are produced in the atmosphere when fossil fuels (coal, fuel oil, natural gas, wood, etc.) are burnt in an insufficient supply of oxygen.

(*ii*) Forest fires, coal refuse burning and agriculture burning also produce a lot of smoke.

(*iii*) Many industries also release carbon particles in the atmosphere.

(*iv*) Carbon particles are also produced in the atmosphere due to inefficient burning of fuel in vehicles.

2. Mists

These are suspensions of liquid particles in air which arise because of chemical reactions and condensation of vapours in air. For example, mists are produced by the particles of the spray liquids. The common examples are portions of herbicides and insecticides which miss their targets and travel through the air to form mists. Similarly, sulphuric acid mist is produced when SO_3 present in the atmosphere comes in contact with moisture.

3. Fumes

These are condensed vapours. For example, fumes are generally produced by the condensation of vapours during sublimation, distillation, boiling and several other chemical reactions. Generally, organic solvents, metals and nonmetallic oxides constitute fumes.

4. Dust

The solid particles (over 1μm in diameter) suspended in the air are called **dust.** These particles enter into atmosphere from natural, domestic and industrial sources. These enter the atmosphere by volcanic eruptions, blowing of dust by wind, mining operations, crushing and grinding, etc. The non-viable dust particulates in the atmosphere consist of ground limestone, sand tailings from floatation pulverised coal, cement, fly ash and silica dust.

These above types of particulates consist of different types of metals and their compounds and organic particulates as discussed below :

(*a*) Metal particles. These are released into the atmosphere by various metal finishing processes. The common metallic particles in air are lead, mercury, chromium, arsenic, zinc, cadmium, nickel, iron, etc. Although these metallic particles are present in air in very small amounts yet some of these are very dangerous to living organisms.

(*b*) Metal oxides. Metal oxides are released into the atmosphere during combustion of fuels containing metallic compounds. For example, particulate Fe_3O_4 is produced by the combustion of coal containing iron pyrite as :

$$3FeS_2 + 8O_2 \longrightarrow Fe_3O_4 + 6SO_2$$

Power plants using vanadium rich residual oil are sources of V_2O_5 pollutants.

(*c*) Metal salts. Burning of coal gives $CaCO_3$ in ash which is partly converted into CaO. Sulphuric acid droplets in the atmosphere combine with basic pollutants CaO or NH_3 to form salt particulates.

$$H_2SO_4 + CaO \longrightarrow CaSO_4 + H_2O$$
$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$$

(*d*) Tetraethyl lead. It is a source of lead salts in the atmosphere. Tetraethyl lead is added to gasoline to improve its antiknocking property. It is oxidised to PbO which tends to deposit on spark plugs and values. This is undesirable and is a source of air pollution.

(*e*) Fly ash. *These are the small ash particles formed by the combustion of fossil fuels which are carried into the air by gases produced during combustion.* These enter into the atmosphere from power plants, smelters and mining operations.

(*f*) Asbestos dust. This originates from industrial units manufacturing asbestos sheets, gaskets, ropes, etc. Asbestos insulation and asbestos flooring also add towards asbestos dust in the atmosphere.

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(*g*) Organic particulate matter. Organic particulates are released in the air when hydrocarbons present in coal and oil are oxidised. Among these polycyclic aromatic hydrocarbons (PAH) containing fused benzene rings are important components of organic particulate because of their carcinogenic nature.

These particles are readily adsorbed on the surface of soot particles present in the atmosphere and therefore are serious health hazards.

Effects of Particulates

The effects of particulate pollutants depend upon the size of the particles. The coarser particles of size more than 5 microns are likely to lodge in the nasal passages whereas the smaller ones are more likely to penetrate into the lungs. The rate of penetration is inversely proportional to the size of the particles. Some of these particles are carcinogens. Continuous inhaling of these small particles for long periods of time irritates the lungs and causes 'scarring' or 'fibrosis' of the lung lining. This type of disease is very common in industrial settings and is known as "**pneumoconiosis".**

Different types of lung diseases are caused by different types of particulates. For example, asbestos causes **asbestosis,** the dust containing silica (SiO_2) causes **silicosis**, the workers working in coal mines suffer from **black lung disease,** whereas textile workers suffer from **white lung disease,** etc.

Lead particulates are highly poisonous and have a serious effect on brain central nervous system and cause cancer.

The suspended particulate matter in the atmosphere reduce visibility and influence weather also. These reduces the amount of light rays reaching the surface of the earth and therefore, lowers the temperature of the earth. By blocking the sunlight, they cause drop in the earth's temperature by providing condensation nuclei, they contribute to increase fog and rain in cities.

The large concentration of these particles spoil many articles and blackens buildings. These particulates have large surface area and hence offer good sites for adsorption of many harmful inorganic and organic matter. Gases like SO_2, PAH particles, toxic metals (Be, Pd, Cd, Cr, etc.) are adsorbed on the surface of soot as shown below.

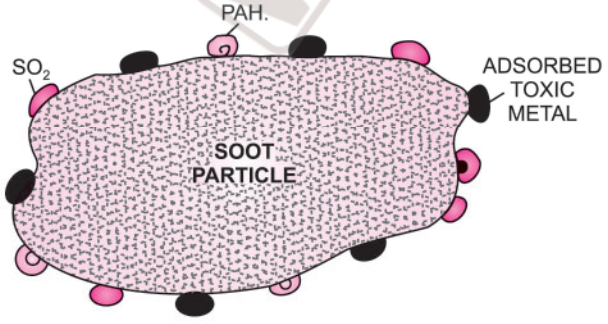

Fig. 4. Soot particle with toxic adsorbates.

Control of Particulates

Various methods are employed to reduce the presence of carbon and other particulates in the atmosphere.

(*i*) Effluent gases from the industries are led into a chamber where the velocities of these gases decrease so that dust or droplets get settled. This method is suitable for particles which are settled readily and is not suitable for the fine particles which require longer settling time.

(*ii*) The carbon and other dust particles are removed by **electrostatic precipitator.** This method is based on the principle that the particles acquire electrical charges when subjected to an electric field. In this method, two electrodes are fitted against the inside walls of the smoke stack (Fig. 5). When high voltage (30,000 – 100,000 V) is applied, an electric discharge takes place across the stack and as a result, air in the stack is ionized. The ionized air consists of ions and free electrons. The free electrons get attached to the gaseous particles moving up the stack. The particles get negatively charged and are attracted to the positive electrode located on the inner wall of the stack and settle down there. These can be dislodged from the electrodes by water or vibration of the electrodes and are collected in a reservoir. In this way about 99% of the particulate matter gets removed from the fuel gases.

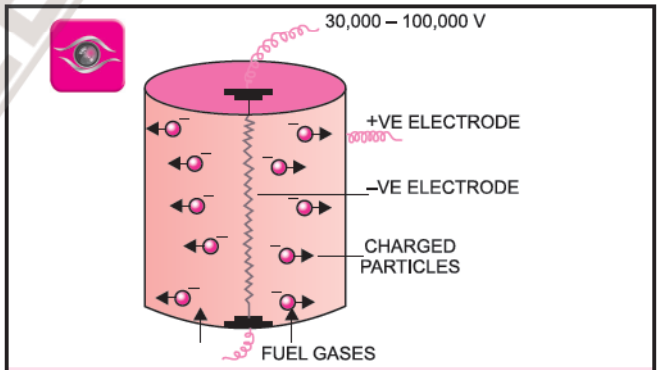

Fig. 5. An electrostatic precipitator.

(*iii*) The solid, liquid or gaseous particulates can be removed by spraying water from spray chambers.

(*iv*) Large amount of particles can be collected in cyclone collectors.

SMOG

Smog is a mixture of smoke, dust particles and small drops of fog. It is a major air pollutant in big cities. This is the best known example of air pollution that occurs in many cities throughout the world. The small drops of smog contains poisonous gases produced by burning of fuels in homes, factories and automobiles.

$$\text{Smoke} + \underset{\text{Containing harmful gases}}{\text{Fog}} \longrightarrow \text{Smog}$$

Smog is of two types :

(*i*) *Classical smog,* and

(*ii*) *Photochemical smog.*

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1. Classical smog

This type of smog is formed by the combination of smoke, dust and fog containing sulphur dioxide from polluted air. It is formed in those areas which have cool and humid climate and where sulphur dioxide in the air is very high. This is also called **chemical smog.** This type of smog was observed in 1962 in London. The city remained covered with smog for 5 days and it caused deaths of many persons. Chemically, it is a reducing mixture so it is also called **reducing smog**.

2. Photochemical smog

This type of smog is formed by the combination of smoke, dust and fog with an air pollutant in the atmosphere as a result of photochemical reaction. It occurs in those areas which have warm, dry and sunny climate. It has high concentration of photochemical oxidants. These are produced when some of the primary pollutants interact under the influence of sunlight. It occurs in warm, dry and sunny climate. It develops in cities in which the atmosphere is loaded with large quantities of automobile exhausts, stagnant air masses and intense sunlight. It has been observed in cities which have sunny, warm and dry climates such as Los Angeles and Denver in U.S.A. Therefore, it was earlier called ***Los Angeles smog***. The photochemical smog is chemically oxidising because it has high concentration of oxidants. It is characterized by brown hazy irritating fumes. As a result of photochemical smog having characteristic brown haze, the cities such as Los Angeles are sometimes called ***brown air cities.***

Formation of photochemical smog

The chemistry of formation of photochemical smog centres around nitric oxide (NO). The formation of photochemical smog can be understood by the following steps :

(*i*) During the early morning before the sun rise, the automobile exhaust emits CO, hydrocarbons and oxides of nitrogen. The NO reacts with oxygen to produce NO_2, a yellowish brown gas.

(*ii*) As the sun rises, ultra-violet and visible radiations fall on the earth. The NO_2 absorbs energy from sunlight and breaks up into nitric oxide and free reactive oxygen atoms.

$$NO_2 \xrightarrow{h\nu} NO + \underset{\text{(Reactive oxygen)}}{O}$$

Some of these oxygen atoms combine with O_2 in the air to produce ozone gas.

$$O_2 + O \longrightarrow O_3$$

Ozone reacts with NO to form NO_2 and O_2

$$O_3 + NO \longrightarrow NO_2 + O_2$$

NO_2 again absorbs U.V. radiations and the entire cycle starts again. Both NO_2 and O_3 are strong oxidizing agents and can react with unburnt hydrocarbons (from exhaust of automobiles) to form organic free radicals. The formation of organic free radicals results into a number of chain reactions producing many undesirable compounds (such as formaldehyde, acrolein, organic peroxides, organic hydroperoxides, peroxyacyl nitrates etc.) which constitute photochemical smog. It also includes H_2O_2. The brownish haze of photochemical smog is largely due to brown colour of NO_2

$$3CH_4 + 2O_3 \longrightarrow \underset{\text{Formaldehyde}}{3HCHO} + 3H_2O$$

Acrolein and peroxyacetylnitrate (PAN) are very noxious substances.

$$\underset{\text{Acrolein}}{CH_2{=}CHCHO} \qquad CH_3{-}\overset{\overset{O}{\|}}{C}{-}OONO_2$$

Peroxyacetylnitrate (PAN)

For example, peroxyacylnitrate (PAN) is a constituent of photochemical smog which irritates eyes. This is formed from aldehydes, in which the reaction is initiated by hydroxyl radical, $OH^{\bullet}$ formed by the reaction of excited atomic oxygen with water, or photolysis of nitrous acid.

$$H_2O + O \longrightarrow 2HO^{\bullet}$$

$$HNO_2 \xrightarrow{h\nu} HO^{\bullet} + NO$$

The $OH^{\bullet}$ leads to the formation of PAN as :

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{OH^{\bullet}} \underset{\text{(Acyl radical)}}{R{-}\overset{\overset{O}{\|}}{C}{\bullet}} \xrightarrow{O_2} \underset{\text{(Peroxyacyl radical)}}{RCOO^{\bullet}}$$

$$\downarrow$$

$$R{-}\overset{\overset{O}{\|}}{C}OONO_2$$

PAN

Harmful effects of Photochemical Smog

The three main components of photochemical smog are ozone, nitrogen oxides and organic derivatives (such as acrolein, formaldehyde, PAN etc.). Each of these have hazardous effects of smog.

1. Pungent smelling smog containing ozone is very toxic. It can cause coughing, wheezing, bronchial constriction and irritation to the respiratory mucous system.

2. Aldehydes and peroxyacylnitrate (PAN) components of photochemical smog cause irritation of eyes and affects respiratory tract of human beings.

3. It reduces visibility causing nose, throat and eye irritation. It may lead to several chronic diseases of eyes, heart and lungs.

4. It affects human health and comfort.

5. Photochemical smog affects plant growth and damages plants. Ozone is known to cause damage to

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vegetation and reduction in plant growth and productivity of crop. PAN has also highest toxicity to plants. It attacks younger leaves and causes bronzing and glazing of their surfaces.

6. Materials are also adversely affected by photochemical smog. For example, rubber has strong affinity for ozone and is cracked and aged by smog.

Control of Photochemical Smog

Efforts are being continuously made to control or reduce the formation of photochemical smog. This can be done by controlling the primary precursors of photochemical smog such as NO_2 and hydrocarbons and the secondary precursors such as ozone and PAN. For this, efficient catalytic converters are designed and installed in the automobiles to reduce photochemical smog because reduce the smog and prevent the release of nitrogen oxides and hydrocarbons to the atmosphere. Certain plants such as Pinus, Juniparus, Quercus, Pyrus and Vitis can metabolise nitrogen dioxide and therefore, plantation of these plants could help to reduce photochemical smog.

Photochemical smog can also be suppressed by certain compounds which trap free radicals. These are sprayed in the atmosphere where they generate free radicals which combine with free radical precursors of photochemical smog and consequently reduce it.

ACID RAIN

Fossil fuels contain compounds of sulphur and nitrogen in addition to carbon. The combustion of fuels contributes significantly to atmospheric pollution. The burning of fossil fuels gives CO_2. The gaseous CO_2 dissolves in water droplets to form weak acid, carbonic acid.

$$CO_2(g) + H_2O(aq) \longrightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Rain water normally has pH of 5.6 due to the formation of H^+ ions from the reaction of rain water with carbon dioxide present in the atmosphere. When the pH of the rain water falls below 5.6, it becomes acidic and is called **acid rain.** Thus, acid rain means the way in which acid from the atmosphere is deposited on the earth's surface.

However, CO_2 is not the major component of acid rain because it is not soluble in water like the oxides of sulphur and nitrogen. The oxides of nitrogen and sulphur undergo many photochemical reactions in atmosphere and form HNO_3 and H_2SO_4 acids. During rains, these acids fall to the earth with rain. This polluted rain is called *acid rain*. The main reactions are :

Nitric acid is formed as :

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + 2O_2 \longrightarrow NO_3 + O_3$$

$$NO_2 + NO_3 \longrightarrow N_2O_5$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

$$\text{or } 4NO_2(g) + O_2 + 2H_2O(l) \longrightarrow 4HNO_3(aq)$$

Similarly, sulphuric acid is formed as :

$$2SO_2(g) + O_2(g) + 2H_2O(l) \xrightarrow[\text{particles}]{\text{Soot}} 2H_2SO_4(aq)$$

Thus, **acid rain is the rain water containing acids such as nitric acid and sulphuric acid which are formed by the oxides of nitrogen and sulphur present in air as pollutants.**

The presence of soot particles in atmosphere speeds up the oxidation process. Due to the presence of HNO_3 and H_2SO_4 in rain the pH of water decreases. Ammonium salts are also formed and can be seen as an atmospheric haze (aerosol of fine particles). Aerosol particles of oxides or ammonium salts in rain drops result in wet deposition. SO_2 is also adsorbed directly on both solid and liquid ground surfaces and this is deposited as dry deposition.

Harmful effects of Acid Rain

Acid rain is very damaging. It is toxic to vegetation, human life and aquatic life. Some of its harmful effects are:

1. It causes extensive damage to buildings and sculptural materials of marble, limestone, slate, etc. These materials react with rain water and get damaged.

$$CaCO_3 + H_2SO_4 \rightleftharpoons CaSO_4 + CO_2 + H_2O$$

As a result of acid rain, the invaluable statues and buildings deteriorate. In Greece and Italy, many invaluable statues have been partially facaded. The Taj Mahal of India is facing the same problem.

2. When acid rain falls and flows as ground water to reach rivers, lakes, etc, it affects plants and animal life in aquatic ecosystem. The acid rain has also caused elimination of life from some fresh water lakes by destroying the living bodies.

3. The rain water also corrodes metals and damages iron and steel structures.

4. Acid rain is harmful for agriculture, trees and plants because it dissolves and washes away nutrients needed for their growth. Therefore, it damages leaves of trees and plants and retard the growth of forests. It also retards the growth of certain crops such as peas, potato, raddish, carrot, beans, spinach, etc.

5. Acid rain dissolves heavy metals from soils, rocks and sediments. The heavy metal ions such as copper, lead, mercury and aluminium leached from the soil enter well water and produce many toxic effects.

6. Acid rain corrodes water conduit pipes resulting in leaching of some heavy metals such as iron, lead and copper into our drinking water which have toxic effects.

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Methods to reduce the formation of acid rain

Acid rain is due to emission of oxides of nitrogen and sulphur in the atmosphere. Therefore, to reduce the formation of acid rain, the emission of these gases has to be controlled. For this, the following steps should be taken :

(*i*) By using fossil fuels having less sulphur content in power plants and industries. For example, natural gas should be used than coal or coal containing lesser sulphur contents should be used.

(*ii*) By using less vehicles driven by fossil fuels.

(*iii*) By using catalytic convertors in cars so that exhaust gases are converted into nitrogen.

(*iv*) By using powdered limestone to neutralise the acidity of the soil.

Acid rain and Taj Mahal of India

The acid causes extensive damage to buildings and sculptural materials of marble, limestone, slate etc. The air in the city of Agra where Taj Mahal is located contains very high levels of oxides of sulphur and nitrogen. This causes acid rain and it reacts with marble ($CaCO_3$) of Taj Mahal

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

As a result, the marble becomes pitted and weakened mechanically because the soluble salts are easily leached out by rain water. Therefore, the wonderful monument is being slowly eaten away and the marble is getting discoloured and lustreless. The same problem is being faced by Greece and Italy where the stone statues have been partially dissolved by acid rain.

To protect Taj Mahal, the Government of India has announced an action plan in 1995 to prevent the disfiguring of this historical wonder. This plan aims at clearing the air in the **Taj Trapezium,** an area which includes towns of Agra, Firozabad, Mathura and Bharatpur. Under this plan about more than 200 industries lying within this trapezium would shift over the use of natural gas or liquefied petroleum gas instead of coal or oil. A new natural gas pipeline would provide more than half a million cubic metres of natural gas a day to this area. The people living in this area will also be encouraged to use LPG in place of coal or kerosene oil. Even the vehicles plying on highways in the nearby areas of Taj Mahal would be encouraged to use diesel of low sulphur content.

STRATOSPHERIC POLLUTION : FORMATION AND DEPLETION OF OZONE LAYER

Ozone is an important constituent of the stratosphere at altitudes between 15 and 25 km. It is formed in the atmosphere by the decomposition of oxygen by ultra-violet radiation from the sun having wavelength shorter than 260 nm.

$$O_2(g) + h\nu \xrightarrow{UV} O(g) + O(g)$$

$$O(g) + O_2(g) \xrightarrow{UV} O_3(g)$$

Most atmospheric ozone is found in stratosphere where its concentration is about 10 ppm (parts per million) by volume. Ozone is thermodynamically unstable and decomposes into molecular oxygen. It has the important photochemical property of absorbing solar radiation between the wavelength of 200 nm and 300 nm.

$$O_3(g) + h\nu \longrightarrow O(g) + O_2(g)$$

The reactive atomic oxygen formed in the above reaction recombines with molecular oxygen to form ozone. This completes the ozone cycle. Thus, a dynamic equilibrium exists between the production and decomposition of ozone molecules

The thick layer of ozone is called **ozone blanket** because it is very effective in absorbing harmful ultra-violet rays given out by the sun. Therefore, the ozone layer is also known as **protective shield.** Since living cells can be destroyed by ultra-violet radiation, the ozone layer protects us from its damaging effects. If there were no ozone in the stratosphere,life on the earth would not be possible. Even a small decrease in the concentration of ozone could lead to an increased incidence of skin cancer.

Depletion of Ozone layer and its effects

Recently in 1980, scientists have observed a hole in the ozone blanket covering the upper atmosphere around Antarctica. Recent observations have also shown that the ozone layer diminishes over the south pole in spring during August-September to a greater extent year after year. This depletion of the protective blanket of ozone will cause a damaging effect because harmful ultra-violet rays can come to earth through this hole. The increased level of ultra-violet rays will result in damage to plants, animals, human beings and even inanimate matter posing great threat to ecosystem over the globe.

Thus, the depletion of ozone layer is a serious threat to mankind. Scientists believe that every 1% decrease in ozone leads to 2% increase in skin cancer due to exposure to sun's ultra-violet rays.

The depletion of ozone may be due to some *natural processes* or *industrial activities.*

Nitrous oxide (N_2O) occurs naturally at very trace levels in stratosphere. It can react with electronically excited oxygen atoms obtained by the ozone cycle to give NO.

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$$N_2O + O^* \longrightarrow \underset{\text{Nitric oxide}}{2NO}$$
(Excited atomic oxygen)

This removes an oxygen atom needed by the ozone cycle and the product, NO can destroy a second ozone molecule which breaks up another cycle.

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$
$$\overline{O_3 + O \longrightarrow 2O_2}$$

Therefore NO is very damaging because just one NO molecule sets up a chain reaction which removes ozone again and again. There are similar ozone depleting chain reactions involving other stratospheric gases.

Chlorofluoro carbons and Ozone layer

Chlorofluoro carbons are compounds such as $CFCl_3$, CF_2Cl_2, CF_3Cl, commonly known as **freons.** These compounds are non-reactive, odourless, non-toxic, non- flammable, and thermally stable.

The large amount of these products are being extensively used in air conditioners, refrigerators, fire fighting materials, fast food packing materials, for sterilizing surgical instruments in medicinal products, in the production of plastic foam and by the electronic industries as cleaning solvents and are released in the atmosphere causing air pollution.

Once chlorofluorocarbons (CFCs) are released in the atmosphere, they mix with the normal atmospheric gases and ultimately reach the stratosphere. In stratosphere, they get broken down by powerful ultraviolet radiations releasing chlorine free radicals ($Cl^\bullet$). These released Cl free radicals cause a catalytic chemical reaction and cause significant depletion of stratospheric ozone layer.

$$CF_2Cl_2 + h\nu \longrightarrow Cl^\bullet + CF_2Cl^\bullet$$

The free radical, $Cl^\bullet$ reacts with O_3 through a chain reaction :

$$Cl^\bullet + O_3 \longrightarrow ClO^\bullet + O_2$$
$$ClO^\bullet + O \longrightarrow Cl^\bullet + O_2$$

These chlorine atoms are free to react with more ozone. As a result, many O_3 molecules can be destroyed for each chlorine atom produced. It has been shown that over one thousand ozone molecules can be destroyed by one Cl. The net result of these reactions is destruction of several molecules of O_3 for each Cl atom produced.

Thus, *CFCs are transporting agents for continuously producing chlorine radicals into the stratosphere and hence damaging the ozone layer.*

Effects of Depletion of the ozone layer

The **depletion of ozone** layer has the following harmful effects :

(*i*) Depletion of ozone layer poses serious threat to mankind. It results in ageing of skin, cataract, sunburn, skin cancer diseases, etc.

(*ii*) Ultra-violet rays may damage immune system which may lead to increased viral infections.

(*iii*) Increased exposure to ultra-violet radiation will damage marine plants, marine animals and fish which form an important part of human food.

(*iv*) These radiations adversely affect the plant proteins which lead to harmful mutation of cells.

(*v*) These also increase the evaporation of surface water through the stomata of the leaves and decrease the moisture content of the soil.

(*vi*) Increase in ultraviolet radiations damage paints and fibres causing them to fade faster.

(*vii*) Freons trap the warmth of the sun and disturb greenhouse effect leading to higher temperature which could damage crops and pose dangers to low lying ocean port cities from increased melting of ice.

Ozone Depletion over Antarctica

The chain reactions described above can occur all over the stratosphere. However, the depletion of ozone layer leading to **ozone hole** has mainly been observed in the stratosphere over Antarctica. In the other parts of the stratosphere, two alternative reactions consume chlorine monoxide and chlorine atoms as :

$$ClO^\bullet + NO_2 \longrightarrow \underset{\text{Chlorine nitrate}}{ClONO_2}$$
$$Cl^\bullet + CH_4 \longrightarrow \dot{C}H_3 + HCl$$

In other words, oxides of nitrogen in the stratosphere scavenge the chlorine monoxide radicals while methane molecules scavenge the chlorine radicals. Thus, these destroy the chain mechanism for the ozone depletion and no ozone hole is created.

However, in Antarctica, the conditions are different. During winters, special types of clouds called **Polar Stratospheric Clouds (PSCs)** are formed over Antarctica. These clouds are of two types :

Type I Clouds. These contain some solidified nitric acid trihydrate ($HNO_3.3H_2O$) form at about 196 K.

Type II Clouds. These contain some ice form at about 188 K.

These two types of clouds play a very important role in ozone depletion. On the surface

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of polar stratospheric clouds, chlorine nitrate formed in the above reaction undergoes two transformations :

(*i*) It gets hydrolysed as :

$$ClONO_2 + H_2O \xrightarrow{\text{hydrolysis}} HOCl + HNO_3$$

(*ii*) It reacts with hydrogen chloride formed during the reaction

$$ClONO_2 + HCl \longrightarrow Cl_2 + HNO_3$$

These HOCl and Cl_2 formed can be reconverted into reactive chlorine atoms even under mild conditions resulting ozone depletion.

The ozone depletion over Antarctica occurs during spring time (from early September to late October) and gets replenished after spring time. During the spring time, the sun begins to shine over Antarctic skies and HOCl and Cl_2 are photolyzed by sunlight according to the following reactions:

$$HOCl + h\nu \longrightarrow OH^{\bullet} + Cl$$
$$Cl_2 + h\nu \longrightarrow 2Cl^{\bullet}$$

These reactive chlorine atoms formed deplete ozone through the chain mechanism reactions. During winters, when Polar Stratospheric Clouds are formed over Antarctica skies, stable patterns of wind cover the continent. This is called **Polar Vortex** which is a tight whirlpool of winds. This is very rigid so that the air within it is isolated from the sun and from the warmer air of the temperate region. Because of this polar vortex surrounding Antarctica, the ozone rich air from the non-polar region is not able to fill the ozone hole. Therefore, Polar Vortex remains intact during the spring. After the spring, the sunlight increases and the vortex breaks down (some time in November) and the ozone rich air from the temperate region fills the ozone hole.

To control this harmful effects of CFCs, serious efforts are being made to control the use of CFCs and find alternative methods. The **Montreal Protocol** signed by 24 countries in October 1987, was the first step to bring down the world production of freons. At some places, these are being replaced by safe substitutes like hydrochlorofluoro carbons (HClFCS) which have only one tenth as destructive effect as CFCs.

GREENHOUSE EFFECT AND GLOBAL WARMING

Carbon dioxide is an essential component of atmosphere and in normal concentrations, it is harmless. However, due to human activities such as burning of fossil fuels like coal, natural gas, petroleum, etc., the amount of CO_2 entering the atmosphere is increasing. The increase in proportions of CO_2 in atmosphere can lead to global warming through greenhouse effect as explained below:

Sun emits light of different wavelengths consisting of ultra-violet, visible region and infra-red. Of these the harmful ultra-violet radiations are absorbed by the ozone layer in the stratosphere. The visible and infra-red radiation pass through the atmosphere and reach the surface of the earth (Fig. 6). However, some of the light incident on earth is reflected back. For example, of the total incoming light that falls upon the Earth, about 50% reaches the surface and is absorbed by it. About 20% of the incoming light is absorbed by gases in the atmosphere, such as ultra-violet (*uv*) light by ozone in stratosphere and infra-red (IR) by CO_2 and water vapour present in air. The remaining 30% is reflected back into space by particulates and other reflecting bodies without being absorbed.

When the earth cools, the energy is re-emitted from the earth's surface in the form of infra-red radiations which are absorbed by CO_2 and water vapour. After the absorption of infra-red radiations by CO_2 and water vapour, these thermal infra-red radiations are re-emitted in all directions and therefore, some are redirected back towards earth's surface and heat up the atmosphere (earth and air). This heating of the earth due to trapped radiations is called **greenhouse effect**.

Thus, ***the warming of the earth or global warming due to re-emission of sun's energy absorbed by the earth followed by its absorption by carbon dioxide molecules and water vapour present near the earth and then its radiation back to the earth is called greenhouse effect.***

The gases which can trap infra-red radiation given by the sun to produce greenhouse effect leading to heating

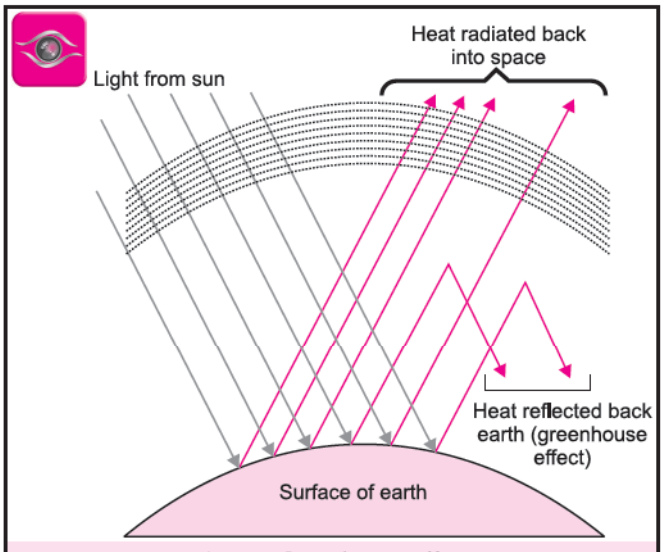

Fig. 6. Greenhouse effect.

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up the environment are called **greenhouse gases.** The principal gases of the atmosphere N_2, O_2 and Ar do not absorb infra-red light. The common atmospheric gases that have predominantly produced green house warming are **CO_2, water vapours (H_2O) and ozone (O_3)**. Out of these, water vapours and ozone do not contribute much to the greenhouse effect of the earth's atmosphere because water vapours are found only near the surface of the earth whereas ozone is present only in the upper atmosphere. On the other hand, carbon dioxide is uniformly distributed in the atmosphere and hence makes major contribution towards the greenhouse effect. Thus, **carbon dioxide is regarded as the most important greenhouse gas.**

The other greenhouse gases whose concentration has been small in atmosphere but have ability to warm the air substantially are CH_4, N_2O, $CFCl_3$, CF_2Cl_2, etc. Their concentration in atmosphere is increasing with the industrialization and air pollution.

Greenhouse gases

CO_2, CH_4, O_3, H_2O vapour, CFCs

This phenomenon has been named greenhouse effect because it is similar to a greenhouse for plants that is generally made to protect the plants from cold in winter. In cold places, flowers, fruits and vegetables are grown in glass covered areas called greenhouse. The sun's radiations can enter through the transparent glass and heat up the soil and the plants. The warm soil and plants re-emit infra-red radiations which are partly, trapped by the glass (opaque to infra red radiations) and therefore remain inside the glasshouse. Hence, the glasshouse holds the energy of the sun trapped inside and keeps it warm. Therefore, greenhouse protects the plants from cold climate during winter in cold countries.

Greenhouse Effect in an Automobile

The heating due to greenhouse effect can also be observed inside an automobile such as a car parked in the sun with all its windows closed. The glass windows of the car allow the sun's rays to enter the car. Some of these rays are reflected from the inside surface of the car in the form of infra-red light. These rays are trapped by glass windows (just like CO_2 layer) and cause the interior of the car to heat up. Hence, the inside of the car becomes considerably hot.

Implications of Greenhouse effect or Global Warming

Modern human activities are releasing large quantities of CO_2 in the atmosphere. The increase in its proportion in the atmosphere can lead to global warming through increased greenhouse effect. The CO_2 level in atmosphere was about 290 ppm in 1870. Over the past hundred years we have released about 3,60,000 million tonnes of CO_2 in the atmosphere and are continuing to do so at an increasing rate. Due to this large scale release of CO_2 in the atmosphere, its level in the atmosphere has increased to about 356 ppm.

Methane (a greenhouse gas) is produced naturally when vegetation is burnt, digested or rotten in the absence of oxygen. Large amounts of methane are released in paddy fields, coal mines, from rotting garbage dumps and by fossil fuels.

Chlorofluoro carbons (CFC's) are also responsible for global warming due to their greater efficiency of absorbing thermal infra-red radiations. Each molecule of CFC has the potential to cause the same extent of global warming as do tens of thousands molecules of CO_2. CFC's are being excessively used in insulating freezers, refrigerators and air conditioners and are posing threat of global warming. However, Government is now trying to control the production of CFCs.

The net effect of increased level of all these greenhouse gases is increased greenhouse effect or global warming which may lead to increased global temperature. The global warming will have drastic effect on the climate and may prove disastrous. If nothing is done to control the concentration of these gases into the atmosphere, than average temperature will increase. It has been observed that the average temperature of the earth has increased by about 1°F due to greenhouse effect. If CO_2 is continued to be released into the atmosphere at the present rate then by the end of this century the earth's average temperature is expected to increase by 3.6°F. This excessive heating of the earth would melt all the snow on poles and different mountains. This would increase the water level of the sea and as a result the cities located on the coastal areas are likely to be flooded.

Effects of increase in global temperature on the climate of the earth

The increase in average global temperature can have the following effects on the climate of the earth :

(*a*) In temperate regions, the summer will be longer and hotter and winter will be shorter and warmer. A warmer climate will make certain cities extremely hot to live.

(*b*) There will be increase in total amount of global rainfall but some regions will receive less rainfall.

(*c*) The number of days having intense showers and high temperatures both will increase.

(*d*) The problem of desertification, drought and soil erosion will become more worse.

(*e*) As a result of rise in temperature of the earth, ocean will get warm up and sea level would rise flooding low lying regions. The increase in sea level would have profound effects on habitation patterns and will threaten to submerge many coastal countries like Bangladesh, Indonesia, Maldives, parts of coastal India and many other island nations.

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(*f*) Increase in greenhouse effect is expected to cause cooling of the stratosphere. This is because most thermal IR radiations will be absorbed at low altitudes and little will be left to warm stratosphere.

(*g*) Tropical storms, hurricanes, etc. will be stronger and more frequent and will cause devastation.

(*h*) Some areas may become more humid or wetter or some other areas will become dry. The tropics may become wetter and the subtropics which are already dry, are expected to be drier.

(*i*) Due to global warming, human health will be affected. Increased number of hot days and extreme weather may cause chronic respiratory diseases. This also causes increase in the incidences of infectious diseases like dengue, malaria, yellow fever, sleeping sickness, etc.

(*j*) Insect carrying diseases such as malaria may also increase.

(*k*) Animal health will also be affected due to spread of diseases by parasites.

(*l*) Ocean temperature change may also affect marine life adversely.

Methods to prevent global warming

Some steps to minimise the release of green house gases and prevent global warming into the atmosphere are :

(*i*) By minimising the use of cars by car pools or taking public transport in cities. This can also be done by preferring walking or using bicycles.

(*ii*) By planting more and more trees and increasing the green cover.

(*iii*) By avoiding the cutting of trees.

(*iv*) By avoiding the burning of dry leaves, etc.

(*v*) By not smoking in public places and work places.

(*vi*) By educating the public about greenhouse effect and the methods to save our environment.

WATER POLLUTION

Water is most plentiful of all the natural sources. It covers nearly three-fourth of the earth's surface in the form of snow over mountains, as a liquid in the rivers, lakes, springs and oceans. Water is very essential for life. Without water there would be no life. It is very essential for the growth of human body and has significant role in industry, agriculture and civilization.

The quality of water especially for drinking purposes has been a vital factor for the human welfare. The pollution of drinking water has frequently caused many water borne diseases and epidemics such as cholera, typhoid fever, etc. Therefore, water pollution is a matter of serious concern for every citizen. The main culprits for water pollutions are domestic waste from urban and rural areas and industrial wastes which are discharged into natural water supplies.

Water pollution may be defined as

the contamination of water by foreign materials which make it harmful for the health of human beings, animals, plants or aquatic life and make it unfit for domestic, industrial or agricultural uses.

The degree of purity required for water depends upon its use. For example, the water polluted for drinking purposes may be satisfactorily used for irrigation or producing electricity at hydroelectric power plant or for cooling purposes.

Pollution of water originates from human activities. Through different paths, pollution reaches surface or ground water. The easily identified source or place of pollution is called point source *e.g.*, Municipal and industrial discharge pipes where the pollutants enter the water source. On the other hand, non-point sources of pollution are those where a source of pollution cannot be easily identified. For example, acid rain, storm water drainage (from streets, parking lots, lawns etc.) agricultural runs off (from farm, animals and crop lands etc.). The major water pollutants and their common sources are given in Table 2.

Table 2. Major Water Pollutants and their Sources.

Pollutant	Sources
Micro-organisms	Domestic sewage
Organic wastes	Domestic sewage, animal manures, food processing wastes, decaying plants and animals, paper discards, rags and other bio degradable wastes
Plant nutrients	Chemical fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Insoluble particles of soil and rock and inorganic and organic compounds which wash into water from mining, agricultural activities, construction activities and soil erosion.
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive wastes	Mining of uranium containing minerals and accidental release from nuclear plants.
Heat	Water used by industrial plants for cooling which is discharged as hot water.

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SOURCES OF WATER POLLUTION

The water pollution may be caused by domestic sewage, industrial effluents, agricultural discharges, sedimentation, radioactive discharges, thermal pollutants etc. The major sources of water pollution are domestic sewage and industrial wastes.

(*i*) Domestic sewage. The domestic sewage contains oils, human excreta, dirt, paper, rags, sand grains, dissolved material such as detergents and inorganic compounds such as sodium chloride, ammonium sulphate and ammonium phosphate, decomposed kitchen waste. The sewage also contains many disease causing bacterias called **pathogens which are most serious water pollutants**.

(*ii*) Industrial wastes. Industrial wastes are also the major source of water pollution. The industrial wastes polluting water are mainly from industries such as coal or ore mines, textile industries, paper industries, food processing industries, dairies, chemical industries, pharma-ceuticals, sugar and distilleries, oil refineries, tanneries, vegetable oil and soap industries etc. These wastes may contain inorganic and organic suspended particles and inorganic and organic soluble matter.

(*iii*) Agricultural discharges. These include fertilizers, pesticides and insecticides, etc. entering the water body.

(*iv*) Sediments. Water can also be polluted by sediments. These are water insoluble particles of soil and rock and many inorganic and organic compounds which wash into water from mining, agricultural activities, construction activities and activities associated with soil erosion. It represents the most extensive pollutants of surface water.

(*v*) Radioactive pollutants. Many radioactive isotopes enter the surface water from geothermal wells or accidental releases from nuclear power plants.

(*vi*) Thermal pollutants. Many processes such as combustion of fuel in boilers, electric power plants and industrial plants produce a lot of heat. Therefore, to cool the various equipments, the water from the nearby rivers, lakes and ocean bays are circulated through the heated parts. The circulating water becomes hot and when this hot water is discharged back to the surface water, it can have many adverse effects. This is called **thermal pollution**.

(*vii*) Oil. Water pollution in seas and rivers is caused by oil due to increased use of oil base technology, excessive off-shore explorations and transportation of oil through water ways. This results from discharge of oil from oil tankers and offshore drilling explorations and accidents, leakage of pipe lines over and under water ways.

TYPES OF WATER POLLUTANTS

1. Pathogens. The most serious water pollutants are the disease causing agents called pathogens.

Pathogens include bacteria and other organisms which enter water from domestic sewage and animal excreta. Human excreta contains bacteria such as **escherichia coli** and **streptococcus faecalis** which cause gastrointestinal diseases. These bacteria can cause great epidemic diseases.

2. Organic wastes. The organic matter such as leaves, grass, trash etc. are also common pollutants. These pollute water as a consequence of run off. Excessive phytoplankton growth within water is also a cause of water pollution. These wastes are biodegradable. The large population of bacteria decompose organic matter present in water.

3. Chemical pollutants. Water being an excellent solvent dissolves many water soluble inorganic chemicals. Some of these pollutants are:

(*i*) Heavy metals. These are metals such as cadmium, lead and mercury which are present in industrial or mining wastes. These metals are poisonous and can be dangerous to humans because our body cannot excrete them. These metals can cause damage to kidneys, liver, central nervous system, etc. For example, cadmium and mercury can cause kidney damage whereas lead poisoning can cause damage to the kidneys, liver, intestines, brain and central nervous system. Mercury poisoning causes a disease called **minamata** in human beings which weakens the muscles and results in weakness in hearing and vision power, mental retardation and paralysis. All of these metals are **cumulative poisons** because the body does not excrete them and their concentration builds up.

(*ii*) Detergents and fertilizers. These may contain phosphates as additives. It may be noted that these do not pose any threat to the aquatic life but serve as nutrients for plants leading to their excessive growth in ponds, lakes and rivers. These encourages the formation of algae which reduces the dissolved oxygen concentration of water. This process of overnutrition is known as **eutrophication.** This impedes the development of higher life forms such as fish.

(*iii*) Petroleum products. Petroleum products also pollute many sources of water. *e.g.*, major oil spills in ocean. This is because of wreckage of oil tankers in open sea or accidents of ships carrying oil in the sea. The spreading of oil into sea is called **oil spill** and the thick layer of oil on the surface of sea water is called **oil slick**. In India an oil spill occurred in Bombay on March 17, 1993 due to rupture of pipeline which damaged the ecosystem and marine life.

(*iv*) Acid polluted water. The acid polluted water having pH less than 3 is deadly to most forms of aquatic life. The water downstream from a mine may

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get contaminated by acid mine drainge formed by microbial oxidation of discarded waste materials at the nine site. The acid mine water mainly contains sulphuric acid produced by the oxidation of iron pyrites (FeS_2). Industrial wastes and acid rain also contribute to the acidic nature of natural water.

(*v*) Polychlorinated biphenyls (PCBs). Polychlorinated biphenyls have very high stabilities and therefore, are finding many applications these days. For example, these are used as fluids in transformers and capacitors, as cleansing solvents, detergents and fertilizers. PCBs are resistant to oxidation and their release into the environment has become a serious pollutant. These are carcinogenic and cause skin disorders in humans. Now a days most of the detergents available are biodegradable. But their use can create other problems. The bacteria responsible for their degradation feed on degradable detergent and grow very rapidly. During their growth, the bacteria may take all the oxygen dissolved in water. As a result of lack of oxygen, other forms of aquatic life such as fish and plants may die. Fertilizers, as we know contain phosphates as additives. The addition of phosphorus in water promotes algae growth. Such a large growth of algae may `cover the water surface. These algae growth often release toxins in water. This bloom infested water will inhibit the growth of other living organisms in the water body. The process of nutrient enrichment of water bodies and subsequent loss of biodiversity is called **eutrophication**.

Until recently, it was a common practice to dump the industrial wastes into nearby stream. These days, this practice has been stopped to prevent stream pollution and to recover some expensive chemicals from these wastes. However, it may be noted that the treatment of industrial wastes is very tedious problem because of the large variety of chemicals present in black liquor coming from the industries.

The treatment of industrial wastes depend upon the nature of the pollutants present.

IMPORTANCE OF DISSOLVED OXYGEN IN WATER

The concentration of dissolved oxygen (DO) in water is very important to support the aquatic life. If the concentration of dissolved oxygen becomes low, the water is said to be polluted. The lower the concentration of dissolved oxygen, the more polluted is the water sample. If the dissolved concentration of oxygen in water is below 6 ppm, the fish growth is inhibited. The two main sources of oxygen are : the oxygen dissolves at the surface of the water from the atmosphere and from photosynthesis carried by many aquatic green plants during day light. It may be noted that still water takes up oxygen slowly whereas turbulent water takes it up more rapidly because bubbles are commonly sumerged. Moreover, at the places where there are many aquatic green plants, the water becomes supersaturated with oxygen during the hours of daylight due to photosynthesis. However, after dark, photosynthesis stops but the plants continue to respire and therefore, the amount of dissolved oxygen decreases. Consequently, during a period of 24 hours, some water samples have considerable amount of dissolved oxygen.

The deoxygenation of water is carried out by various processes. For example, the dissolved oxygen in water is consumed rapidly by micro-organisms to oxidise organic matter of sewage.

$$\underset{\text{From organic matter}}{[CH_2O]\,(aq)} + O_2\,(aq) \xrightarrow{\text{Micro-organisms}} CO_2\,(aq) + H_2O(l)$$

If the concentration of the dissolved oxygen is not restored either by the turbulent flow of shallow water or by a reaction, it is not able to support many organisms. The dissolved oxygen in water is also consumed by the biooxidation of the nitrogenous material.

$$NH_4^+\,(aq) + 2O_2\,(aq) \longrightarrow 2H^+\,(aq) + NO_3^-\,(aq) + H_2O(l)$$

and by the chemical or biochemical oxidation of chemical reducing agents.

$$4Fe^{2+}\,(aq) + O_2\,(aq) + 10\,H_2O\,(l) \longrightarrow 4Fe(OH)_3\,(s) + 8\,H^+\,(aq)$$

$$2SO_3^{2-}\,(aq) + O_2\,(aq) \longrightarrow 2SO_4^{2-}\,(aq)$$

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

The organic waste can be broken down by both aerobic and anaerobic bacteria which act under different conditions. **Aerobic bacteria** are oxygen consuming decomposers which bring about the oxidation of degradable organic matter into carbon dioxide, nitrates, sulphates, phosphates, etc. As a result of aerobic oxidation, dissolved oxygen in the water decreases. Due to short supply of oxygen, the aquatic organisms especially fish and shell fish die from suffocation. Complete oxygen removal kills many other forms of aquatic life except anaerobic bacteria which do not require oxygen.

On the other hand, **anaerobic bacteria** do not require oxygen for the decomposition of organic wastes. The decomposition of organic waste by anaerobic bacteria produce toxic and foul smelling substances such as hydrogen sulphide, ammonia, methane, phosphine, ammonium sulphide, etc. This kind of oxidation of sewage is called anaerobic oxidation.

Dissolved oxygen is an essential requirement of aquatic life *i.e.* animal and plant population in water. The quantity of oxygen consuming wastes in water is usually determined by measuring the **biological oxygen demand** (B.O.D). It is defined as the

amount of oxygen required by microorganisms (bacteria) to break down the organic matter present in a certain volume of a sample of water.

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The amount of BOD in water is a measure of the amount of organic material in water, in terms of how much oxygen will be required to break it down biologically.

The carbon of organic matter is converted into CO_2 and since 1 mol of C requires 1 mol of oxygen, BOD is directly related to the concentration of organic matter. Therefore, the high value of BOD. indicates that water is polluted. Therefore, the BOD is taken as a realistic measure of water quality. **The clean water would have a BOD value of less than 5 ppm whereas BOD of 17 ppm or more indicate highly polluted water.**

In order to measure BOD, the water sample is first saturated with oxygen. It is then incubated at constant temperature (usually 20°C) for 5 days. This allows time for micro-organisms in water sample to oxidise organic matter. The remaining oxygen is determined and the difference gives the amount of oxygen consumed by micro-organisms for decomposition i.e., BOD.

There is another parameter called **chemical oxygen demand** (COD). Certain chemicals other than organic wastes also react with dissolved oxygen in water. This is referred as **chemical oxygen demand (COD).** Thus, BOD measures the oxygen consumed by living organisms assimilating organic matter present in waste while COD is a measure of biological oxidisable as well as biological inert organic matter such as cellulose. Thus, if BOD or COD values of water are large, it indicates that water is heavily polluted.

In order to measure COD, the given water sample is treated with a known quantity of an oxidising agent (potassium dichromate, $K_2Cr_2O_7$) in acidic medium. This oxidises most of the polluting substances including those which are resistant to microbial oxidation. The excess of $K_2Cr_2O_7$ is determined by back titration with a suitable reducing agent such as Mohr's salt. From the concentration of $K_2Cr_2O_7$ consumed, the amount of oxygen used in oxidation may be calculated using the following chemical equation :

$$K_2Cr_2O_7\,(aq) + 4H_2SO_4\,(aq) \longrightarrow K_2SO_4\,(aq) + Cr_2(SO_4)_3\,(aq) + 4H_2O\,(l) + 3O\,(aq)$$

The results are expressed in terms of amount of oxygen in ppm that would be required to oxidise the contaminants. This is called COD.

WATER QUALITY PARAMETERS AND INTERNATIONAL STANDARDS

The quality of water is of vital concern for mankind because it is directly linked with human welfare. The main requirements for drinking water are :

The drinking water should be fit for human consumption having the following essential parameters for water quality :

(*i*) It should be colourless and odourless.

(*ii*) It should be pleasant in taste.

Table 3. Permissible Limits of Drinking Water.

Parameter	Permissible limits (ppm)	Ill-effects of pollutants
Dissolved Oxygen	250	—
(pH)	5.5–9.5	
Arsenic	0.05	Cramps, paralysis
Barium	1.0	Toxic to heart
Cadmium	0.005	Anaemic, kidney dysfunction
Chromium	0.05	Carcinogenic
Fluoride	1–1.5	Skeleton disorder, nervous breakdown and mottling of teeth enamel
Lead	0.05	Anaemic, kidney dysfunction, nervous
Aluminium	0.2	disorder, brain damage
Selenium	0.01	Toxic at high levels
Copper	3.0	Toxic to plants and algae
Mercury	0.001	Highly toxic, mental disorders and death
Zinc	5.0	Toxic
Alkyl benzene-sulphonate	0.5	Irritation of the gastrointestinal tract
Chloride	600	Harms agricultural crops
Sulphate	500	Laxative and hypertension
Pesticides	0.005	Toxic, carcinogenic, kidney dysfunction

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(*iii*) It should be clear and turbidity should be less 10 ppm.

(*iv*) Its pH should be between 5.5 to 9.5.

(*v*) The total dissolved solids should not be more than 500 ppm.

(*vi*) It should be free from disease causing micro-organisms.

(*vii*) It should be reasonably soft.

(*viii*) It should be free from objectionable chemicals.

There are some international standards for drinking water which must always be obeyed if water is to be used for drinking purposes. The parameters and standards for water quality and harmful effects of pollutants beyond permissible limits are given in Table 3 for some common chemicals. Some of these are also briefly discussed below :

1. Fluoride. Soluble fluoride is normally added to drinking water and its concentration should be upto 1–1.5 ppm or 1–1.5 mg dm^{-3}. This limit is within agreed safety limits and protects teeth against decay. The deficiency for this compound in drinking water is harmpul to man and causes diseases such as tooth decay, etc. The F^- ions make the enamel on teeth much harder, by converting hydroxyapatite $[3Ca_3(PO_4)_2 . Ca(OH)_2]$ the enamel on the surface of the teeth into harder fluorapatite $[(3Ca_3 (PO_4)_2. CaF_2]$. However, F^- ion concentration above 2ppm causes brown mottling of teeth. Higher concentrations of fluoride are poisonous and are harmful to teeth and bones at levels above 10 ppm (mg dm^{-3}). This problem has been reported from some parts of Rajasthan.

2. pH. The pH of the drinking water should be between 5.5 to 9.5. A decrease in pH of the water increases the solubility of the heavy metal ions.

3. Sulphate. Sulphate is harmless at moderate concentrations but excessive concentration of sulphate above 500 pm produces laxative effects and hypertension.

4. Nitrate. Excessive nitrate in drinking water is also harmful and can cause ***methemoglobinemia*** (blue baby syndrome). It is linked to stomach cancer. The maximum limit of nitrate ion in drining water is 50 ppm.

5. Lead. Lead pipes are very commonly used for water transport and is liable to get contaminated with lead, particularly when water is acidic. The permissible limit for lead ions in drinking water is 50 ppb (µg dm^{-3}). Excessive lead cause anaemia, kidney dysfunction, nervous disorder, brain damage etc.

6. Other metals. The maximum permissible limit recommended of common metals in drinking water and their ill effects are given alongside.

Table 4. Maximum prescribed concentration of some metals in drinking water.

Metal	Maximum Concentration (ppm or mg dm^{-3})
Iron, Fe	0.2
Manganese, Mn	0.05
Aluminium, Al	0.2
Copper, Cu	3.0
Zinc, Zn	5.0
Cadmium, Cd	0.005

R.U. Curious...

❑ **Certain newly born babies develop illness known as blue baby syndrome.**

▶ Blue baby syndrome or simply known as blue baby is a term used to describe the infants with blue tinted skin. This may be caused by excessive nitrate (NO_3^-) ions in drinking water in some rural area having high levels of nitrates present in ground water. When consumed, the nitrates get reduced to nitrite ions in the digestive system. The nitrites react with oxyhemoglobin (the oxygen carrying blood protein) to form methemoglobin, which cannot carry oxygen. As a result, the oxygen carrying capacity of blood gets reduced and the organs, cells, tissues or skin may be deprived of oxygen, causing infants to develop blue baby syndrome. This can be fatal if left untreated leading to even death. This condition is also known as **methemoglobinemia**.

SOIL POLLUTION OR LAND POLLUTION

Soil receives large quantities of hazardous wastes from different sources and gets polluted.

Any factor which deteriorates the quality, texture and mineral content of the soil and disturbs the biological balance of the organisms in it and has lethal effect on the plant growth is called **soil pollutant.**

India being agricultural based economy gives high priority to agriculture. The production of agriculture depends primarily on the quality of soil because it is the soil which provides nutrients, water and minerals for the growth of plants. However, India is also facing serious problem of deteriorating quality of soil and resulting into soil pollution. The main sources of soil pollution are dumping of industrial wastes, urban wastes, volatile organic compounds, radio-active wastes and agricultural practices. Among these modern agricultural practices pollute the soil to a large extent. With the increasing use of fertilizers, pesticides, herbicides, weedicides and soil conditioning agents to increase the crop yield, the soil pollution problems have also been increased.

Fertilizers contaminate the soil with impurities which come from raw materials during their

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manufactures. For example, As, Pb and Cd present in rock phosphate mineral get transferred to superphosphate fertilizers. Since the metals are not degradable, these get accumulated in the soil due to the excessive use of phosphate fertilizers. Similarly, some metal ions such as Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+} etc. are added to the soil in trace amounts as micronutrients. However, excessive addition of these micronutrients may lead to their accumulation above the toxic level. These may also cause soil pollution.

Different kinds of pesticides are used to control pests in the crops. Though these pesticides help in getting boost in food production, yet the excessive use has been of great concern because these cause soil pollution. These pose a potential danger to the human health because eating of food contaminated with these chemicals may cause serious problems. Consequently, many of these chemicals have been banned or restricted in use.

Thus, the role of pesticides in protecting crops and generating pollution is very significant and discussed below :

Role of Pesticides in generating Pollution

The chemicals which are used for destroying pests are called **pesticides.** These are used to kill or control unwanted dangerous species of plants and animals. Pesticides are basically synthetic toxic chemicals with ecological repercussions. The repeated use of the same or similar pesticides make some pests resistant to that group of pesticides, thereby, making the pesticides uneffective. For example, when insect resistance of DDT increased, other organic toxins such as Aldrin and Dieldrin, etc. were introduced. Most of the organic toxins are water insoluble and non-biodegradable. Therefore, these high persistent toxins are transferred from lower trophic level to higher trophic level through food chain. Over the time, the concentration of toxins in higher animals reach a level which causes serious metabolic and physiological disorders. In response to high persistence of chlorinated organic toxins, a new series of less persistent or more biodegradable products have been introduced. These are **organo-phosphates** and **carbamates**. But these chemicals are severe nerve toxins and hence are more harmful to human beings. There are some reports of pesticides related deaths of agricultural field workers.

The pesticides may be classified in following categories:

1. Insecticides

These are used to kill insects in agricultural fields. During world war II, DDT [2,2 (bis-p-chlorophenyl)-1,1,1- trichloroethane] was found to be of great use in controlling malaria and other insect borne diseases. Therefore, after the war, DDT was used in agriculture to control the damages caused by in sects, rodents, weeds and various crop diseases. Other common examples of insecticides are : malathion, carbaryl, BHC. Among these DDT (dichloro diphenyl trichloro ethane) is an organo chlorine compound. Organo chlorine compounds are stable in the environment, toxic to insects in small amounts but much less so to humans, because they are not very soluble in water. These are persistent and show their biological activity for long periods of time. However, these insecticides by accumulating in the environment affect many non target organisms in addition to the target pests.

2. Herbicides

These are used to kill weeds or undesirable vegetations. For example : sodium chlorate ($NaClO_3$), sodium arsenate ($NaAsO_3$),2,4 dichlorophenoxy acid, triazines, etc. Most herbicides are toxic to mammals but are not as persistent as organo-chlorides. These chemicals decompose in a few months. Like organo-chlorides, these also become concentrated in the food web. Same herbicides cause birth defects.

3. Fungicides

These are used to control the growth of various types of fungus and check plant diseases. For example, thiram $(CH_3)_2$ NCSS, phenyl mercury acetate, bordeaux mixture. Generally, organic compounds of mercury have been used as fungicides. However, these compounds break down in soil and these have disastrous consequences. In Iraq many deaths were reported in 1971-72 resulted from the people eating bread made from grain that had been treated by fungicide methyl mercury.

4. Rodenticides

These are used to kill rodents (rats and mice). For example : warfarin, zinc phosphate.

In addition pesticides also include *nematicides* (which inhibit nematodes), *molluscicides* used to kill molluscs mainly snails and slugs), *piscicides* (used to control undesirable fish species and other aquatic animals).

A major Air Pollution Accident—Bhopal Gas Tragedy

A major air pollution accident took place on the night of December 2, 1984 in Bhopal (Madhya Pradesh in the Union Carbide Factory. This is known as **Bhopal gas tragedy**. On the chilly night, when the city of Bhopal was virtually asleep, at about 11.30 pm a dense cloud of deadly methyl isocyanate (MIC) gas leaked from a storage tank of Union Carbide Ltd. plant. This caused intense aching in the eyes of people around the factory. This resulted into deaths of thousands of people and many suffered permanent medical disability. Many women were badly affected and the worst victims being pregnant women.

Methyl isocyanate (MIC) was used to manufacture the insecticide, carbaryl marked under the commercial name **sevin** in this plant. It was prepared by the reaction of methylamine and phosgene.

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$$\underset{\text{Phosgene}}{CH_3NH_2 + COCl_2} \longrightarrow \underset{\text{MIC}}{CH_3N = C = O} + 2HCl$$

MIC is stored in refrigerated moisture free tanks in Union Carbide Factory. It is very sensitive to moisture and itself is a volatile liquid (b.p. 43.45°C). It has been investigated that probably pressure rose in one of the tanks and opened its release value thereby allowing methyl isocyanate to escape into the atmosphere. As the clouds of methyl isocyanate rose over the city, it caused immense loss of life and injury to people. It proved to be a big tragedy.

Monitoring and Control of Pesticide Pollution

Excessive use of pesticides pose a potential hazard to man, animal, fish, vegetations, etc. These spread most widely and alarming danger to the environment. The use of many toxic pesticides have been banned. India is one of the few producers of DDT in the world, which has been banned by USA since 1972 for environmental reasons.

STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTION

To protect human life and lives of plants and other animals, scientists are working hard to plan certain strategies for control of environmental pollution. In addition to solid waste which we see in our household garbage bins, there are medical, industrial, agricultural and mining wastes. The improper disposal of wastes is one of the major causes of environmental pollution. Therefore, the management of wastes is of prime importance. Let us briefly study the methods to control other types of pollution caused by different sources. This involves two common strategies :

A : Management of waste

B : Green chemistry.

A. MANAGEMENT OF WASTE

The production and improper disposal of domestic and industrial wastes are responsible for environmental pollution. The domestic waste includes sewage and municipal waste while industrial wastes include inorganic and organic suspended particles and inorganic and organic soluble matter.

Management of Industrial Waste.

Most industries produce one or more unwanted by products which must be discarded. The problem of solid waste disposal is one of the most serious problem facing our society today.

Industrial solid wastes are sorted out as biodegradable and non-biodegradable wastes.

Biodegradable wastes are generated by food processing units, cotton mills, paper mills and textile factories.

Non-biodegradable wastes are generated by many industrial processes such as:

(*i*) thermal plants produce fly ash

(*ii*) iron and steel plants produce blast furnace slag and steel melting slag.

(*iii*) industries manufacturing aluminium, zinc, copper, etc, produce mud and tailings.

(*iv*) fertilizer industries produe gypsum.

(*v*) industries dealing with metals, chemicals, drugs, pharmaceuticals, dyes, rubber, goods, etc. produce hazardous wastes such as inflammables, composite explosives or highly reactive species.

The disposal of non-biodegradable industrial solid wastes, is very essential. If it is not done by a proper and suitable method it may cause serious threat to the environment. New innovative methods have been designed to make use of waste materials. Great care has to be taken for the disposal of toxic wastes. For example, nowadays, fly ash and slag from the steel industry are used in the cement industry. Large amounts of toxic and hazardous wastes are destroyed by controlled incineration whereas small quantities are burnt along with factory garbage in open bins. Moreover, solid wastes if not managed effectively will affect the components of environment.

Management of Domestic waste.

The best way to manage domestic wastes are to collect these in small bins which are transferred to community bins by private or municipal workers. From these community bins, the wastes are collected and carried to disposable sites. At these sites the wastes are separated into biodegradable and non-biodegradable wastes. Non-biodegradable waste meterials such as glass, plastic, metal scraps, etc. are sent for recycling whereas biodegradable wastes are dumped in land fills and are converted into compost.

If the waste is not collected in garbage bins, it goes into the sewers. Some of it is eaten by dogs and cattles. Non-biodegradable wastes (polythene bags, metals scraps etc.) choke the sewers and cause inconvenience and problems. Polythene bags, if swallowed by cattle can cause their death also. The poor management of waste causes health problems leading to epidemics due to contamination of ground water. It is specially dangerous for those who are in direct contact with the waste such as rag pickers and workers involved in waste disposal because these persons handle waste materials mostly without protective devices such as gloves or water proof boots and gas masks. **We are responsible for their lives.**

Therefore, the normal practice is that all the domestic wastes should be properly collected and

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disposed. These wastes are treated in the following ways :

1. Recycling

This is a simplest method in which the waste is recycled. When the materials are recycled, it saves on the cost of raw materials as well as reduces the costs of waste disposals. Some common examples of recycling by industries are :

(*i*) the collection and recycling of glass

(*ii*) the use of scrap metal in the manufacture of steel

(*iii*) recovery of energy from burning combustible waste.

(*iv*) the use of waste paper

In other words, *recycling converts waste into wealth.*

2. Sewage treatment

The sewage treatment involves the following three types of stages :

1. The **first stage** known as **primary treatment** involves the removal of large solid particles. This is done by mechanical process consisting of **screening** and **sedimentation.** For this, the waste is filtered through different types of screens. The solids that are removed are disposed off in land fill sites. It is then allowed to flow into sedimentation tanks. This process allows the removal of solids that settle out (called **sludge).** This process also allows the removal of grease which floats to the surface and can be skimmed off.

2. The **second stage** known as **secondary treatment** involves the biological oxidation of organic content of waste materials by micro-organisms followed by filtration.

3. The **third stage** also known as final treatment is a series of specialized physical and chemical processes that reduce the quantities of specific pollutants left after primary and secondary treatments. These improve the quality of waste water. The processes commonly used in this treatment ore chemical removal of phosphate, coagulation, filtration, treatment with activated charcoal, disinfection by chlorine, reverse osmosis, etc.

During these operations sludge is produced which also poses a problem for safe disposal. The sludge is dried and then may be incinerated, digested or damped as explained below :

***(a)* Incineration**

This converts organic materials into CO_2 and water. This is used for household waste, chemical waste and biological waste (e.g. from hospitals). Such treatment is carried out under aerobic conditions in the presence of plentiful supply of oxygen and at very high temperature (above 1273 K). The exhaust gases are filtered. This process reduces the volume of the waste and inorganic ash is left behind which is disposed of as land fill.

$$\text{Organic waste} + O_2 \xrightarrow[> 1273\ K]{\text{Aerobic conditions}} CO_2 + H_2O$$

This method disposes of the relatively inert PCBs (polychlorobenzenes) and the high temperature generated allows the endothermic reactions such as destruction of C–Cl bonds in organochlorine compounds. The main disadvantage of this process is that it causes air pollution. Moreover, the ash from the municipal incinerators is very finely divided and can be ingested into the lungs. Incomplete combustion of PCBs can cause formation of highly toxic chloro compounds such as polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs).

***(b)* Digestion**

The sewage sludge can undergo anaerobic digestion when micro-organisms degrade wastes in the absence of oxygen. This process can also be used to degrade a variety of toxic organic wastes. The products of digestion are carbon dioxide and methane, which may be used as a fuel.

$$2\begin{bmatrix}\text{Organic waste}\\ \text{C, H, O}\end{bmatrix} \longrightarrow CO_2\,(g) + CH_4\,(g)$$

(*c*) Dumping

This is widely used practice of dumping the sewage sludge in the nearby seas. It is known as ocean dumping. However, the application of sludge to the land is increasing. The sludge contains nitrogen and phosphorus which may be useful as a fertilizer. Urban areas produce sludge which contains many toxic substances, so the amount of such sludge dumped in this way must be carefully controlled.

B. GREEN CHEMISTRY AS AN ALTERNATIVE TOOL FOR REDUCING AIR POLLUTION

We have learnt that increasing population, increased use of fossil fuels and increasing number of industries and vehicles are polluting our environment to an alarming extent. The increase in pollution adversely affects the health of humans and other living organisms. As we know self sufficiency in food has been achieved in India since late 20th century by using fertilizers and pesticides and developing improved methods of farming, good quality of seeds, irrigation etc. But over exploitation of soil and excessive use of fertilizers and pesticides have resulted into deterioration of soil, water and air.

With the growing awareness of the environmental pollution, the international community is under increasing pressure to find methods to save our lives from the increasing pollution. This does not mean that we should stop the process of advancement that has been set in but to search methods which would help in reduction of pollution of our environment. The scientists are searching new alternatives which do not cause environmental pollution. This new approach is

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called **Green Chemistry** which was introduced in early 1990s. It means zero discharge of toxic, persistent substances, into the environment guaranted by the fact that they are never produced. **Green chemistry** may be defined as

a strategy to design chemical processes and products that reduces or eliminates the use and generation of hazardous substances.

This would bring about minimum pollution or deterioration to the environment. In other words, green chemistry aims to virtually eliminate toxic, persistent substances from the environment by ensuring their no further releases and destroying existing deposits of these chemicals. So, green chemistry means environmental friendly or no pollution. For example, we have been using organic solvents such as benzene, toluene, carbon tetrachloride, etc. as a media for many reactions. These are highly toxic. Now, scientists are planning greener alternative to use water or non polluting solvents as a medium in place of organic solvents. Similarly, instead of using synthetic materials for packing, green chemistry plans to use environmental friendly recyclable or safely disposable materials.

Green chemistry also requires change in our habits and life-style. These days many green products are available in the market in developed countries.

BASIC AIMS OF GREEN CHEMISTRY

Since the inception of green chemistry, scientists from all over the world are using the creative and innovative skills to develop new synthetic methods, new processes, analytical tools, reaction conditions, catalysts, etc. **So, green chemistry prevents problems before they occur by designing new approaches.** Green chemistry considers the full life cycle impacts of a product at the initial design stage. The **basic aims** of green chemistry are :

(*i*) Reformulation of synthetic routes so that hazardous substances do not enter into the atmosphere.

(*ii*) During synthesis, care must be taken to select starting materials that can be converted into end products with allmost 100% yield. This can be achieved by arriving at optimum conditions of synthesis.

(*iii*) The methods used to obtain starting materials *e.g.* mining, refining, etc. should have minimum impact on the natural environment.

(*iv*) New routes for the production of green chemicals and materials.

(*v*) The development of environmentally improved methods for the existing industrial processes. The material inputs should be of low or no toxicity or at least reduced toxicity compared with the traditional method.

(*vi*) The use of starting materials–reagents and solvents that pose less hazard to man and his environment.

(*vii*) The synthetic reactions may preferably be carried out in aqueous medium because water has high specific heat and low volatility. Water is cost effective, non-inflammable and does not have any carcinogenic effects.

(*viii*) The raw materials and methods should produce less waste to avoid their treatment and problem of disposal.

(*ix*) The use of renewable rather than depleting resources wherever possible.

(*x*) The use of biotechnological alternatives.

(*xi*) New methods and tools for evaluating environmental impact.

(*xii*) The awareness among common man to use green products.

Green chemistry in Day-to-Day Life

Some common examples of green chemistry in our day-to-day life are:

(*i*) Dry cleaning of clothes.

Tetrachloroethene ($Cl_2C = CCl_2$) has earlier used as solvent for dry cleaning. This compound is suspected to be carcinogenic and contaminates the ground water. The process of using this compound has now been replaced by a new process in which liquefied carbon dioxide alongwith suitable detergent is used. This causes less harm to ground water. Replacement of halogenated solvent by liquid CO_2 will result in less harm to ground water.

Similarly, hydrogen peroxide (H_2O_2) is used for the purpose of bleaching clothes in the process of laundry. This gives better results and makes use of less water, therefore, saving a lot of water. It is also not harmful.

(*ii*) Bleaching of paper

Chlorine gas was used earlier for bleaching paper, which is highly toxic chemical. Its use has been replaced by hydrogen peroxide with a suitable catalyst which promotes the bleaching action of hydrogen peroxide.

(*iii*) Synthesis of chemicals.

Ethanal (CH_3CHO) is commercially prepared nowadays by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium:

$$\underset{\text{Ethene}}{CH_2=CH_2} + O_2 \xrightarrow[\text{in water}]{\text{Catalyst Pd(II),Cu(II)}} \underset{\text{Etanal}}{CH_3CHO}(90\%)$$

The yield is about 90.0%.

Thus, we can say that green chemistry is a cost effective approach which involves reduction in material, energy consumption and waste generation.

Always remember environment protection begins with us.

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To save our environment, we all as human beings have to think seriously. If we follow some basic steps as an individual to keep our environment pollution free, we can contribute significantly towards a better quality of our environment and human life.

* Always set up a compost pit in your garden or any other place in your home and use it to produce manure for your plants. This will reduce the use of fertilizers.
* Always use a cloth bag instead of plastic carry bags when you buy vegetables, fruits, groceries or any other item.
* Take care that all newspapers, glass, aluminium and other items in your area are recycled.
* We must realize that though we donot have solutions for every problem but we can concentrate on issues and try to find their proper solutions.
* We should always take care to put into practice whatever we preach.

Always remember, environmetal protection begins with us.

add on Conceptual Questions

CONCEPTUAL QA

Q.1. Explain giving reasons "the presence of CO reduces the amount of the haemoglobin available in the blood for carrying oxygen to the body cells".

Ans. CO is a poisonous gas and it binds to haemoglobin of the blood more readily (about 200 times) than oxygen to form carboxy haemoglobin.

$$Hb + CO \rightleftharpoons HbCO$$

Carboxy haemoglobin

The presence of CO, therefore, reduces the amount of the haemoglobin available in the blood for the transport of oxygen to the body cells.

Q.2. Fish do not always grow as well in warm water as in cold water. Why ?

Ans. The amount of dissolved oxygen in warm water is less than in cold water.

Q.3. Name four major Greenhouse gases.

Ans. (*i*) Carbon dioxide (*ii*) Methane (*iii*) Ozone (*iv*) Chlorofluorocarbon compounds.

Q.4. Why is acid rain considered as a threat to Taj Mahal ?

Ans. Taj Mahal is made of marble. The acid rain contains H_2SO_4 which attacks the marble ($CaCO_3$):

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

As a result, the marble becomes pitted and weakened mechanically. Therefore, the monument is being slowly eaten away and the marble is getting discoloured and lustreless.

Q.5. Why does the rain water normally have a pH of about 5.6 ? When does it become acid rain ?

Ans. Normally rain water has a pH of about 5.6 due to the dissolution of CO_2 of the atmosphere into it :

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3$$

$$H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-}$$

When the pH of rain water falls below 5.6, it becomes acid rain.

Q.6. What is pneumoconiosis ? How does it occur ?

Ans. Pneumoconiosis is a disease of lung which is caused due to inhalation of small particles (mist, smoke, fumes and dust). These particles irritate the lungs and exposure of such particles for long periods of time causes scarring or fibrosis of the lung lining.

Q.7. Name the gas which caused Bhopal Gas Tragedy.

Ans. Methyl isocyanate (CH_3 N = C = O) or MIC.

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Q.8. Name four tropospheric pollutants.

Ans. The tropospheric pollutants may be gaseous or particulate. For example,

Gaseous : Oxides of sulphur, Oxides of nitrogen

Particulate : Dust, Smoke.

Q.9. What is the major cause of ozone layer destruction ?

Ans. The major cause of ozone layer destruction is the release of chlorofluorocarbon compounds (CFCs) know as freons in the atmosphere.

Q.10. List main differences between classical smog and photochemical smog.

Ans. The main difference between classical smog and photochemical smog are :

Classical smog	Photochemical smog
1. This is formed due to buildup of sulphur oxides and particulate matter from fuel combustion.	1. This is formed due to photochemical reaction of sunlight on the nitrogen oxides and hydrocarbons produced by automobiles and factories.
2. It involves smoke and fog.	2. It does not involve any smoke or fog.
3. It occurs in cool humid climate (in winter).	3. It occurs in warm, dry and sunny climate (in summer).
4. This type of smog was first observed in London in 1952.	4. This type of smog was first observed in Los Angeles in 1950.
5. It has high concentration of SO_2 and, therefore, is reducing in character.	5. It has high concentration of oxidising agents and, therefore, is oxidising in character.
6. It causes bronchitis and irritation *i.e.*, problems in lungs.	6. It causes irritation in eyes.

Q. 11. What is the importance of measuring BOD of a water body?

Ans. BOD is the measure of level of pollution caused by organic biodegradable material in a water body. The clean water would have a BOD value of less than 5 ppm whereas higher values of BOD indicate polluted water.

Q. 12. Define eutrophication.

Ans. The process of nutrient enrichment of water bodies and subsequent loss of biodiversity is called eutrophication.

Chapter Summary

Key Terms

- **Contaminant:** A substance which does not occur in nature but is introduced by human activity into the atmosphere effecting its composition.
- **Pollution:** The addition of any foreign material or any physical change occurring in nature which may harm or affect living organisms directly or indirectly.
- **Smog:** A combination of smoke and fog laced with SO_2
- **Acid rain** Rain water containing acids such as H_2SO_4 and HNO_3 and has pH of 4–5.
- **Greenhouse effect:** Global warming due to re-emision of sun's energy absorbed by earth followed by its absorption by CO_2 molecules and water vapour near the earth and then radiation back to the earth.
- **Green chemistry:** A strategy to eliminate toxic, persistent substances from the environment.

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QUICK CHAPTER ROUND UP

AIR POLLUTANTS

Primary pollutants
- harmful chemical substance that directly enters the air

Secondary pollutants
- harmful chemical substance that is formed in the air by chemical reactions

Common air pollutants
- CO, SO_2, NO, NO_2 H_2S, Cl_2, NH_3, hydrocarbons, particulates, chlorofluorocarbons

$\Rightarrow$ **CO is the major air pollutant**

SMOG
- is a mixture of smoke and fog.
- **Classical smog:** formed by the combination of smoke, dust and fog containing sulphur dioxide from polluted air.
- **Photochemical smog:** formed by the combination of smoke, dust and fog with an air pollutant in the atmosphere as a result of photochemical reaction.
- **Peroxyacylnitrate (PAN)** is a constituent of photochemical smog.

$$R-\underset{\underset{O}{\|}}{C}OONO_2$$

ACID RAIN
- When the pH of the rain water falls below 5.6, it becomes acidic and is called **acid rain.**
- It is rain water containing acids such as HNO_3 and H_2SO_4 which are formed by the oxides of nitrogen and sulphur present in air as pollutants.

- Acid rain reacts with statues made of marble, limestone, etc. Acid rain reacts with marble ($CaCO_3$).

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

- As a result, the marble becomes pitted and weakened mechanically because the soluble salts are easily leached out by rain water.
- **Acid rain attacks marble of Taj Mahal of Agra.**

OZONE BLANKET
- The thick layer of ozone is called ***ozone blanket*** because it absorbs harmful ultra-violet rays given out by the sun. Therefore, the ozone layer is also known as **protective shield.**
- The ozone layer is getting depleted due to some natural processes or industrial activities
- The depletion of ozone layer is because of its reactions with chlorofluorocarbons (CFC)

GREEN HOUSE EFFECT
- The warming of the earth or global warming due to re-emission of sun's energy absorbed by the earth followed by its absorption by carbon dioxide molecules and water vapour present near the earth and then its radiation back to the earth is called greenhouse effect.

▸ Green house gases are
CO_2, CH_4, O_3, H_2O vapour, CFCs

WATER POLLUTION

- Water can be polluted by pathogens, heavy metals and pesticides

BOD & COD
- Amount of oxygen required by microorganisms to break down the organic matter present in certain volume of a sample of water is called biochemical oxygen demand, BOD
- Chemical oxygen demand (COD) is a measure of biological oxidisable as well as biological inert organic matter
- Clean water would have BOD value <5 ppm while BOD of >17 indicates highly polluted water.

Contaminants in Water
- pH of drinking water should be between 5.5. to 9.5.
- F^- ion concentration should be upto 1 – 1.5 ppm.
- F^- ions make the enamel on teeth harder by converting $[3Ca_3(PO_4)_2.Ca(OH)_2]$ to $[3Ca_3(PO_4)_2.CaF_2]$
- Excessive concentration of sulphate above 500 ppm produces laxative effects.
- Excessive nitrate causes methemoglobinemia **(blue baby syndrome)**.
- Excessive lead causes anaemia, kidney dysfunction, brain damage.

Pesticides
- **Insecticides.** DDT, malathion, carbaryl, BHC
- **Herbicides.** Sodium chlorate, sodium arsenate, 2, 4-dichlorophenoxy acid, triazines
- **Fungicides.** Thiram, phenyl mercury acetate, bordeaux mixture
- **Rodenticides.** Warfarin, zinc phosphate

- **Green chemistry** is a strategy to eliminate toxic, persistent substances from the environment.

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NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. Define environmental chemistry.

Ans. Environmental chemistry is defined as the branch of science which deals with study of origin, transport, reactions, effects and fates of chemical species in the environment. It deals with social, economical, biological, physical and chemical interrelations with our surroundings.

Q. 2. Explain tropospheric pollution in 100 words.

Ans. The tropospheric pollution occurs because of the presence of undesirable gaseous and solid particles in the air. The main pollutants in the troposphere are as follows:

(*i*) **Gaseous air pollutants**. The gaseous air pollutants include oxides of sulphur (SO_2, SO_3), nitrogen (NO, NO_2), carbon (CO, CO_2), hydrogen sulphide (H_2S), hydrocarbons, ozone and other oxidants.

(*ii*) **Particulate pollutants:** These pollutants are dust, fumes, mist, spray, smoke, etc.

Q. 3. Carbon monoxide gas in more dangerous than carbon dioxide gas. Why?

Ans. Carbon monoxide is a poisonous gas and it binds to haemoglobin of the blood more readily (about 200 times) than oxygen to form carboxy haemoglobin.

$$Hb + CO \rightleftharpoons HbCO$$

Carboxy haemoglobin

The presence of CO, therefore, reduces the amount of haemoglobin available in the blood for the transport of oxygen to the body cells. The harmful effects of enhaling increasing amounts of CO include reduction in awarness of judgement, dizziness, weak eye sight, headache, nervousness and cardiovascular disorders. At higher concentrations of CO, suffocation, loss of consciousness or even death after several hours. However, CO_2 does not combine with haemoglobin and hence is less harmful pollutant. CO_2 is main contributor towards, green house effect and global warming.

Q.4. List gases which are responsible for greenhouse effect.

Ans. CO_2 is the main gas which causes greenhouse effect. Other greenhouse gases are methane, ozone, water vapour, nitrous oxide, chlorofluorocarbons (CFC's).

Q. 5. Statues and monuments in India are affected by acid rain. How?

Ans. The air around statues and monuments in India contains fairly high concentrations of oxides of sulphur and nitrogen. This is mainly because of a large number of industries and power plants in the nearby areas. The presence of these oxides cause acid rain. This acid rain causes extensive damage to statues and monuments because limestone reacts with rain water and gets damaged.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O$$

(From acid rain)

As a result, these monuments are being slowly eaten away and the marble gets discoloured and lusterless.

Q. 6. What is smog? How is classical smog different from photochemical smog?

Ans. Smog is a major air pollutant in big cities. It is a mixture of smoke, dust particles and small drops of fog.

Smoke + Fog $\longrightarrow$ Smog

Differences between classical and photochemical smog. *Refer Conceptual Questions, Q, 10 (Page 28).*

Q. 7. Write down the reactions involved during the formation of photochemical smog.

Ans. *Refer Text page 12.*

Q. 8. What are the harmful effects of photochemical smog and how can they be controlled?

Ans. *Refer Text page 12.*

Q. 9. What are the reactions involved for ozone layer depletion in the stratosphere?

Ans. *Refer Text page 15.*

Q. 10. What do you mean by ozone hole? What are its consequences?

Ans. *Refer Text page 15–16.*

Q. 11. What are the major causes of water pollution? Explain.

Ans. *Refer Text page 19.*

Q. 12. Have you ever observed any water pollution in your area? What measures would you suggest to control it?

Ans. *Please try yourself.*

Q. 13. What do you mean by Biochemical Oxygen Demand (BOD)?

Ans. *Refer Text page 20-21.*

Q. 14. Do you observe any soil pollution in your neighbourhood? What efforts will you make for controlling the soil pollution?

Ans. *Please try yourself.*

Q. 15. What are pesticides and herbicides? Explain giving examples.

Ans. Pesticides are synthetic chemicals used for destroying pests. These are used to kill or destroy unwanted dangerous species of plants and animals. These are basically synthetic toxic chemicals with ecological repercursions. The repeated use of the same or similar pesticides make some pests resistant to that group of pesticides, thereby, making the pesticides

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uneffective. For example, when insect resistance of DDT increased, other organic toxines such as Aldrin and Dieldrin, etc. were introduced. Most of the organic toxins are water insoluble and non-biodegradable. Therefore, these high persistent toxins are transferred from lower trophic level to higher trophic level through food chain. Over the time, the concentration of toxins in higher animals reach a level which causes serious metabolic and physiological disorders. Herbicides are used to kill weeds or undesirable vegetations. For example, sodium chlorate ($NaClO_3$), sodium arsenate ($NaAsO_3$), 2, 4 dichlorophenoxy acid, triazines, etc.

Q. 16. What do you mean by green chemistry? How will it help decrease environmental pollution?

Ans. *Refer Text pages 25-26.*

Q. 17. What would have happended if the green-house gases were totally missing in the earth's atmosphere? Discuss.

Ans. The solar energy radiated back from the earth surface is absorbed by greenhouse gases such as CO_2, CH_4, O_3, CFC's, water vapour, etc. present near the earths surface. Therefore, they heat up the atmosphere near the earths surface and keep it warm. Therefore, they keep the temperature of earth constant and help in growth of plants and existence of life on earth. If there are no greenhouse gases, there would have no vegetation on earth and hence no life on earth.

Q. 18. A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

Ans. Excessive phytoplanktons (*i.e.*, organic pollutants such as leaves, grass, trash, etc.) present in water is biodegradable. A large population of bacteria decompose this organic matter in water. As a result, they consume the oxygen dissolved in water and therefore, the concentration of dissolved oxygen becomes low. If the concentration of dissolved oxygen in water becomes below 6 ppm, the survival of fish becomes difficult. Hence the fish die and float dead on lake.

Q. 19. How can domestic waste be used as manure?

Ans. Domestic wastes consist of two types of materials; biodegradable such as leaves, rotten food, etc.and non-biodegradable such as glass, plastic, metal scrap, etc. The non-biodegradable waste is sent to industry for recycling. On the other hand, the biodegradable waste should be deposited in the land fills on the nearby areas. With the passage of time, it gets converted into useful manure (compost).

Q. 20. For your agricultural field or garden you have developed a compost producing pit. Discuss the process in the light of bad odour, flies and recycling of wastes for a good produce.

Ans. The compost is very useful for agriculture as a fertilizer. But the compost producing pits may give bad odour and flies. Therefore, the compost producing pit should be set up at a suitable place or in a tin to protect ourselves from bad odour and flies. It must be kept covered so that flies connot enter into it and there is not much of bad odour.

NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 41*

Subjective Questions

Short Answer Questions *Carrying 2 or 3 marks*

Q. 1. Green house effect leads to global warming. Which substances are responsible for green house effect?

Ans. The heating of earth due to trapping of radiation is called green house effect. The gas such as CO_2, CH_4, N_2O, $CFCl_3$, CF_2Cl_2, O_3 etc. trap these radiations and are called greenhouse gases.

Q. 2. Acid rain is known to contain some acids. Name these acids and where from they come in rain?

Ans. Acid rain contains acids such as HNO_3, H_2SO_4 and H_2CO_3 (alongwith small amount of HCl).
HNO_3 is formed by the oxidation of NO present in air to NO_2 and NO_3 and subsequent dissolution in water.
H_2SO_4 is formed by the oxidation of SO_2 present in air to SO_3 and subsequent dissolution in water.
H_2CO_3 is formed by the dissolution of CO_2 of the air in water.

Q. 3. Ozone is a toxic gas and is a strong oxidising agent even then its presence in the stratosphere is very important. Explain what would happen if ozone from this region completely removed ?

Ans. Ozone is an important constituent of the stratosphere. Ozone layer acts as a protective blanket or protective shield because it is very effective in absorbing harmful ultra-violet rays given by the sun. Since living cells can be destroyed by ultra-violet radiations, the ozone layer protects us from its damaging effects.

Q. 4. Dissolved oxygen in water is very important for aquatic life. What processes are responsible for the reduction of dissolved oxygen in water?

Ans. The discharge of human sewage and organic waste from paper and pulp industries and leaves, grass, trash etc. in water result in growth of phytoplanktons. These micro-organisms which decompose this organic matter require oxygen. As a result, amount of oxygen in water of lakes, etc. decreases.

Q. 5. On the basis of chemical reactions involved, explain how do chlorofluorocarbons cause thinning of ozone layer in stratosphere.

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Ans. Chlorofluorocarbons are stable compounds. They move to stratosphere by random diffusion. These undergo decomposition in the presence of sunlight to release Cl atoms. These Cl atoms cause catalytic chemical reactions and cause significant depletion of ozone layer as shown below :

$$CF_2Cl_2 \xrightarrow{h\nu} Cl^{\bullet} + CF_2Cl^{\bullet}$$

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O \longrightarrow Cl^{\bullet} + O_2$$

Q. 6. What could be the harmful effects of improper management of industrial and domestic solid waste in a city?

Ans. If the domestic waste in a city is not properly managed, it may go into sewers or may be eaten up by the cattle.
The non-biodegradable waste such as polythene bags, metal scraps, etc may block the sewers. The polythene bags if swallowed by the cattle can result in their death.
Similarly, if industrial waste is not properly managed, it will cause pollution of air, water and soil.

Q. 7. During an educational trip, a student of botony saw a beautiful lake in a village. She collected many plants from that area. She noticed that villagers were washing clothes around the lake and at some places waste material from houses was destroying its beauty.
After few years, she visited the same lake again. She was surprised to find that the lake was covered with algae, stinking smell was coming out and its water had become unusable. Can you explain the reason for this condition of the lake?

Ans. The inflow of domestic waste from houses and fertilizer of plants and the entry of soaps and detergents result into accumulation of phosphate in water. As a result, formation of algae increases which covers the water surface and concentration of dissolved oxygen decreases. Hence a process called eutrophication occurs.

Q. 8. What are biodegradable and non-biodegradable pollutants?

Ans. Biodegradable pollutants are those which can be decomposed by bacteria. For example, dust particles, sewage, cow dung etc.
Non-biodegradable pollutants are those which cannot be decomposed by bacteria. For example, plastic materials, mercury, aluminium, DDT, etc.

Q. 9. What are the sources of dissolved oxygen in water?

Ans. The main sources of dissolved oxygen in water are :
(*i*) Photosynthesis (*ii*) Natural aeration
(*iii*) Mechanical aeration

Q. 10. What is the importance of measuring BOD of a water body?

Ans. BOD is the measure of level of pollution caused by organic biodegradable material in a water body. The clean water would have a BOD value of less than 5 ppm whereas higher values of BOD indicate polluted water.

Q. 11. Why does water covered with excessive algal growth become polluted?

Ans. Presence of excessive algal growth shows that water contains a lot of phosphate due to inflow of fertilizers, etc from the surroundings. Hence, such a sample of water is polluted.

Q. 12. A factory was started near a village. Suddenly villagers started feeling the presence of irritating vapours in the village and cases of headache, chest pain, cough, dryness of throat and breathing problems increased. Villagers blamed the emissions from the chimney of the factory for such problems. Explain what could have happened. Give chemical reactions for the support of your explanation.

Ans. The symptoms observed in villagers show the presence of oxides of nitrogen and sulphur in the environment. These must be coming out of the chimney of the factory. This is due to the combustion of fossil fuels such as coal, oil, natural gas, gasoline etc. to produce high temperature at which oxidation of atmospheric nitrogen takes place forming nitric oxide (NO) and nitrogen dioxide (NO_2) as:

$$N_2 + O_2 \overset{1200\text{–}1750^\circ C}{\rightleftharpoons} 2NO$$

$$2NO + O_2 \overset{1100^\circ C}{\rightleftharpoons} 2NO_2$$

The sulphur present in coal and fuel oil on combustion gives SO_2. Sulphur dioxide is also produced by the roasting of sulphide ores such as copper pyrite ($CuFeS_2$), iron pyrite (FeS_2), copper glance (Cu_2S) etc.

$$Cu_2S + O_2 \longrightarrow 2Cu + SO_2$$

$$2FeS_2 + 5O_2 \longrightarrow 2FeO + 4SO_2$$

Q. 13. Oxidation of sulphur dioxide into sulphur trioxide in the absence of a catalyst is a slow process but this oxidation occurs easily in the atmosphere. Explain how does this happen. Give chemical reactions for the conversion of SO_2 into SO_3.

Ans. The conversion of sulphur dioxide into sulphur trioxide is catalysed by the presence of particulates in the air.

$$2SO_2 + O_2 \xrightarrow{\text{Particulates}} 2SO_3$$

Q. 14. From where does ozone come in the photochemical smog?

Ans. In the presence of sunlight, ultra violet rays convert NO_2 present in air to NO and atomic oxygen. Some of the oxygen atoms combine with O_2 in the air to form ozone.

$$NO_2 \xrightarrow[\text{radiation}]{\text{U.V.}} NO + O$$

$$O_2 + O \longrightarrow O_3$$

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Q. 15. How is ozone produced in stratosphere?

Ans. Ozone in stratosphere is formed by the photochemical reaction of oxygen as:

$$O_2 \xrightarrow{h\nu} O + O$$
$$O + O_2 \longrightarrow O_3$$

Q. 16. Ozone is a gas heavier than air. Why does ozone layer not settle down near the earth?

Ans. Ozone layer is formed in the stratosphere at an altitude of 25 – 30 km from the earth's surface. At this altitude, the force of gravity is negligible and therefore, ozone layer does not settle down.

Q. 17. Some time ago formation of polar stratospheric clouds was reported over Antarctica. Why were these formed? What happens when such clouds break up by warmth of sunlight?

Ans. *Refer text (page 17-18).*

Q. 18. A person was using water supplied by Municipality. Due to shortage of water he started using underground water. He felt laxative effect. What could be the cause?

Ans. The laxative effect is observed only when the concentration of sulphates in water is greater than 500 ppm. Sulphate is harmless at moderate concentration but concentration above 500 ppm produces laxative effects and hypertension.

Long Answer Questions *Carrying 5 marks*

Q. 19. How can you apply green chemistry for the following:

(i) to control photochemical smog.

(ii) to avoid use of halogenated solvents in drycleaning and that of chlorine in bleaching.

(iii) to reduce use of synthetic detergents,

(iv) to reduce the consumption of petrol and diesel.

Ans. (*i*) *Refer Text (Page 25).*

(*ii*) *Refer Text (Page 26).*

(*iii*) Soaps should be used in place of synthetic detergents because soaps are 100% biodegradable and donot cause any pollution problems. Nowadays, soft detergents are available which are biodegradable and hence these may be used.

(*iv*) CNG (Condensed Natural Gas) may be used because it causes less pollution and electrical vehicles which have zero pollution should be used.

Q. 20. Green plants use carbon dioxide for photosynthesis and return oxygen to the atmosphere, even then carbon dioxide is considered to be responsible for green house effect. Explain why?

Ans. The amount of CO_2 produced due to human activities such as burning of fossil fuels (coal, natural gas, petroleum, etc.) and production of lime from limestone is much more than that consumed during photosynthesis. Moreover, consumption in photosynthesis has further decreased due to deforestation.

Q. 21. Explain how does green house effect cause global warming.

Ans. *Refer Text (Page 16).*

Q. 22. A farmer was using pesticides on his farm. He used the produce of his farm as food for rearing fishes. He was told that fishes were not fit for human consumption because large amount of pesticides had accumulated in the tissues of fishes. Explain how did this happen?

Ans. The pesticides travelled from the soil into the crops produced by the farmer. From the crops, used as food for fish, the pesticides entered into water from where they finally entered into the bodies of the fishes. Therefore, the fishes were not fit for human consumption.

Q. 23. For dry cleaning, in the place of tetrachloroethene, liquefied carbon dioxide with suitable detergent is an alternative solvent. What type of harm to the environment will be prevented by stopping use of tetrachloroethene? Will use of liquefied carbon dioxide with detergent be completely safe from the point of view of pollution? Explain.

Ans. Tetrachloroethene ($Cl_2C = CCl_2$) has earlier been used as a solvent for dry cleaning. This compound is suspected to be carcinogenic and contaminates the ground water. This harmful effect has not been prevented by using liquefied CO_2 alongwith suitable detergent.

However, use of liquefied CO_2 with detergent will not be completely safe because detergents also cause pollution, as most of the detergents are non-biodegradable. Moreover, liquefied CO_2 will ultimately enter into the atmosphere and add to greenhouse effect.

QUICK MEMORY TEST

A. Say True or False

1. Acid rain is due to the presence of oxides of sulphur in air.
2. Classical smog is reducing in nature.
3. Ozone is present in stratosphere of the atmosphere.
4. N_2 and O_2 are the two main greenhouse gases.
5. Excess sulphate in water causes blue baby syndrome.
6. The clean water would have a BOD value of more than 17.
7. Fish grows better in warm water than in cold water.
8. The major cause of ozone layer destruction is the release of freons in the atmosphere.
9. Mercury is a biodegradable pollutant.
10. Mesosphere is higher than stratosphere.

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B. Complete the missing links

1. Carbon monoxide combines with haemoglobin of red blood corpuscles to form ..... .
2. The abbreviation PAN stands for ..... .
3. London smog is ..... in nature.
4. The gas leaked in *Bhopal gas tragedy* was ..... .
5. Acid rain contains ..... and ..... and has pH of ..... .
6. The loss of green colour in plants due to the presence of even a low concentration of SO_2 is called ..... .
7. The amount of dissolved oxygen needed by aerobic bacteria to break down the organic matter is called ..... .
8. The process of nutrient enrichment of water bodies and subsequent loss of biodiversity is called ..... .
9. The heating of earth due to trapped radiation is called ..... .
10. Anything which is affected by the pollutants is called ..... .

C. Choose the correct alternative

1. Carboxyhaemoglobin is *more / less* stable than oxyhaemoglobin.
2. Mercury is a *biodegradable / non-biodegradable* pollutant.
3. When pH of rain becomes *more / less* than 5.6, it becomes acid rain.
4. Photochemical smog is *oxidising / reducing* in nature.
5. Major pollutant in air is *CO / SO_2*.
6. Natural decay of animal and vegetable matter is the main source of *H_2S / NO* air pollutant.
7. The main greenhouse gas is *SO_2 / CO_2*.
8. Chlorofluorocarbons *cause damage / prevent damage* of ozone layer.
9. Water having BOD value of 5 ppm is *highly polluted / clean* water.
10. The region of stratosphere is *above / below* troposphere.

Answers QUICK MEMORY TEST

A. Say True or False

1. **False :** Acid rain is due to the oxides of sulphur and nitrogen in the air.
2. True
3. True
4. False
5. **False:** Excessive nitrate causes blue baby syndrome.
6. False
7. False
8. True
9. **False :** Mercury is a non-biodegradable pollutant
10. True.

B. Complete the missing links

1. carboxyhaemoglobin
2. peroxyacyl nitrates
3. reducing
4. methyl isocyanate
5. sulphuric acid, nitric acid, 4 to 5.
6. chlorosis
7. biological oxygen demand (BOD)
8. eutrophication
9. greenhouse effect
10. receptor.

C. Choose the correct alternative

1. more
2. non-biodegradable
3. less
4. oxidising
5. CO
6. H_2S
7. CO_2
8. cause damage
9. clean
10. above.

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Define pollutant.
2. Why is carbon monoxide a pollutant although it is a colourless and odourless gas ?
3. Name two gaseous air pollutants.
4. Which region of atmosphere contains ozone ?
5. Define environmental chemistry.
6. Name two greenhouse gases.
7. Name four regions of atmosphere.
8. Name major air pollutant.
9. Why is ozone called protective shield ?
10. What is an ionosphere ? What does it contain ?
11. What is greenhouse effect ?
12. Name two oxides of nitrogen which are pollutants in the atmosphere.
13. What is photochemical smog ?
14. What is PAN ?
15. Why is CO a potentially dangerous air pollutant ?
16. Name two highly toxic compounds of mercury.
17. Why is CO a very harmful pollutant of air ?
18. List two health problems caused by SO_2.

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19. Name the compounds which cause the depletion of ozone layer.
20. How is ozone formed in the atmosphere ?
21. How does CO_2 cause environmental pollution ?

Short Answer Questions *Carrying 2 or 3 marks*

1. What is environmental chemistry ? Discuss its social relevance.
2. What is the difference between pollutant and contaminant?
3. Discuss the sources, sinks of CO as air pollutant. How is this pollution controlled ?
4. What is the difference between the primary and secondary pollutants ? Give examples.
5. How can internal combustion engines be modified to make auto exhaust free from pollutants ?
6. What is the major air pollutant ? Give its important sources and its harmful effects on human life.
7. Carbon monoxide is more dangerous than carbon dioxide gas. Explain.
8. Explain giving reasons "the presence of CO reduces the amount of haemoglobin av ailable in the blood for carying oxygen to the body cells".
9. Discuss the effect of particulate pollution on human life.
10. What is photochemical smog ? discuss the possible mechanism of its formation.
11. What is acid rain ? What are its harmful effects ?
12. How does oxygen reach water ? How is the oxygen content of a sample of water measured ?
13. What do you understand by the term eutrophication? How does it threaten the development of fish ?
14. What is pneumoconiosis ? How does it occur ?
15. What are smogs ? Distinguish between classical and photochemical smogs.
16. How does SO_2 cause pollution ? Explain as to how this can be checked.
17. Define the terms : Pollutant, contaminate, source and sink. Give one example of each.
18. What is acid rain ? Describe its role in environmental pollution.
19. Write brief account of air pollution caused by oxides of nitrogen.
20. "Carbon dioxide is non-toxic but it is an important environmental problem facing us at present." Comment on the statement.
21. Giving equations explain how does nitrous oxide present in atmosphere cause depletion of ozone.
22. Why is the use of chlorofluoro carbons being discouraged ? Explain.
23. What do you understand by Greenhouse effect ? What are the major Greenhouse gases ?
24. Explain the difference between primary and secondary pollutants.
25. What is green chemistry ? Explain.
26. Give harmful effects of depletion of ozone layer.
27. The depletion of ozone layer occurs over Antarctica during spring time and it gets replenished after spring time. Explain.
28. Why is acid rain considered a threat to Taj Mahal ?
29. Why does the rain water normally have a *p*H of about 5.6 ? When does it become acid rain?
30. Give a brief account of chemical reactions occurring in atmosphere.
31. Write down the reactions involved during the formation of photochemical smog.
32. What are harmful effects of photochemical smog and how can they be controlled ?
33. What are the reactions involved for ozone depletion in stratosphere ?
34. What are pesticides and herbicides ? Explain giving examples.
35. What do you mean by green chemistry ? How will it help to decrease environmental pollution ?
36. What are major causes of water pollution ? Explain.
37. How do chemical industries cause environmental pollution ?
38. What pollutants are released by motor vehicles ? How can we minimize damage caused by them ?
39. What do you understand by BOD and COD ? How are these determined ?
40. What do you understand by
    (*i*) Polar stratospheric clouds (*ii*) Polar vortex
41. Define an environmental pollutant. What do you understand by an environmental pollution model ?
42. What is the cause of acid rain ? How is it harmful to environment ?
43. Why does greenhouse effect lead to global warming ? What could be the consequences of global warming ?
44. Write a short note on Bhopal Gas tragedy ?
45. Fish do not always grows as well as in warm as in cold water, why ?
46. "Oxygen plays a key role in the troposphere while ozone in the stratosphere" Explain.
47. What do you understand by ozone hole ? What are its consequences ? Why does it occur mainly over Antarctica ?

Long Answer Questions *Carrying 5 marks*

1. Discuss the various regions of the atmosphere. Explain the different chemical reactions occurring in the atmosphere.
2. What is air pollution ? Explain briefly the major atmospheric pollutants.
3. How is ozone formed in the atmosphere ? What are the causes of depletion of ozone layer ? Explain harmful effects of depletion of ozone layer.
4. What is greenhouse effect ? What are its effects ?
5. Write short notes on :
   (*a*) Acid rain
   (*b*) Green chemistry as an alternative tool for reducing pollution.

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6. Discuss the sources , sinks of carbon monoxide as an air pollutant. How is this pollution controlled ?
7. Discuss briefly the pollution caused by oxides of sulphur and nitrogen.
8. Write short notes on :
   (*i*) Smog
   (*ii*) Depletion of ozone layer
   (*iii*) Greenhouse effect.
9. Discuss five major water pollutants giving their sources.
10. Explain the following :
    (*i*) Smoke (*ii*) Fumes (*iii*) Dust (*iv*) Mist
11. Explain how does green house effect cause global warming.
12. How can you apply green chemistry for the following :
    (*a*) to reduce the consumption of petrol and diesel.
    (*b*) to control photochemical smog.
    (*c*) to reduce use of synthetic detergents.
    (*d*) to avoid use of halogenated solvents in drycleaning and that of chlorine in bleaching.

Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

CHEMICAL AND PHOTOCHEMICAL REACTIONS IN ATMOSPHERE

Many chemical reactions are occurring in atmosphere in which oxygen plays an important role. Some of these reactions occur by the absorption of solar radiation and these reactions are called **photochemical reactions.** These chemical and photochemical reactions play a significant role in governing the chemical species present in the atmosphere. It may be noted that there are large variations in the atmosphere with regards to composition, temperature, humidity and intensity of sunlight. Therefore, different types of reactions are observed under varying atmospheric conditions.

Oxygen in the troposphere plays an important role in the processes occurring on the earth's surface. For example, oxygen is taking part in burning of fossil fuels.

$$\underset{\text{(Natural gas)}}{CH_4} + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Atmospheric oxygen is also used by aerobic organisms in the degradation of organic material or in oxidation of weathering processes.

$$\text{Organic matter} + O_2 \xrightarrow{\text{Organisms}} CO_2 + H_2O$$

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$

The carbon dioxide and water present in the atmosphere are used by green plants in the presence of sunlight in the process of **photosynthesis** as :

$$6CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2$$

During photosynthesis, oxygen is again returned to the atmosphere.

In the upper atmosphere, oxygen exists in some forms which are different from those stable at lower levels. Thus, in addition to O_2 (molecular oxygen), the upper atmosphere also have O (atomic oxygen), O_2^* (excited molecular oxygen), O^* (excited atomic oxygen), O^+ (ionic oxygen) and O_3 (ozone).

The atomic oxygen is produced by photochemical dissociation of oxygen by ultraviolet radiation ($E = h\nu$).

$$O_2 + h\nu \longrightarrow O + O$$

Due to the above photochemical dissociation of O_2, molecular O_2 is virtually non-existent at very high altitudes. At altitudes exceeding 40 km only less than 10% of oxygen is present as molecular oxygen. The atomic oxygen combines in the presence of radiation to form excited oxygen atom according to the reaction

$$O + O + O \xrightarrow{h\nu} O_2 + O^*$$

The excited oxygen atom gives out visible light at 636 nm, 630 nm and 558 nm wavelength and is responsible for **air glow.** Oxygen ions (O^+) are formed when ultraviolet radiations react with oxygen atom

$$O + h\nu \longrightarrow O^+ + e^-$$

The oxygen ion is present in some regions of the ionosphere. It may be noted that the region beyond stratosphere is dominated by +ve ions such as O^+, O_2^+, NO^+ and free electrons. It is called **ionosphere.** O^+ ion also undergoes a number of other reactions such as

$$O^+ + O_2 \longrightarrow O_2^+ + O$$

$$\underset{\text{(From atmosphere)}}{O^+ + N_2} \longrightarrow NO^+ + N$$

O_2^+ may also be formed according to the reaction

$$N_2^+ + O_2 \longrightarrow N_2 + O_2^+$$

Ozone is present in the stratosphere which acts as a protective radiation shield for living organisms on earth. It is formed by photochemical reactions of oxygen as :

$$O_2 + h\nu \longrightarrow O + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

Where M is another species like a molecule of N_2 or O_2. It absorbs the excess energy liberated by the above reactions and hence stabilize the O_3 molecule. Ozone strongly absorbs ultraviolet light in the region of 220– 330 nm according to the following reactions :

$$O_3 + h\nu \longrightarrow O_2 + O$$

$$O_3 + O \longrightarrow O_2 + O_2$$

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Atomic oxygen may also be eliminated by the reaction

$$O + O + M \longrightarrow O_2 + M$$

Ozone in the stratosphere is destroyed by reaction with reactive hydroxyl radicals or nitric oxide, etc.

$$O_3 + HO^{\bullet} \longrightarrow O_2 + HOO^{\bullet}$$

(Hydroxyl radical)

$$HOO^{\bullet} + O \longrightarrow HO^{\bullet} + O_2$$

Similarly,

$$O_3 + NO \longrightarrow NO_2 + O_2$$

Nitric oxide

$$NO_2 + O \longrightarrow NO + O_2$$

Nitric oxide is produced in the stratosphere below 30 km by the reaction of nitrous oxide (N_2O) with excited oxygen atoms. Nitrous oxide originates from the microbiological processes occurring in the atmosphere.

$$NO_2 + O^* \longrightarrow 2NO$$

Above 30 km in the stratosphere it is produced by ionizing radiation on nitrogen

$$N_2 + h\nu \longrightarrow N + N$$

$$O_2 + N \longrightarrow NO + O$$

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Air Pollution

A1. The major air pollutant is :
(a) CO (b) Oxides of nitrogen
(c) Soot (d) Oxides of sulphur.

A2. The region closest to earth's surface is :
(a) stratosphere (b) mesosphere
(c) troposphere (d) thermosphere.

A3. The major source of CO pollution is :
(a) industrial processes (b) vehicular exhaust
(c) forest fires (d) volcanic activity.

A4. Increased concentration of CO_2 in atmosphere is responsible for :
(a) greenhouse effect (b) acid rain
(c) lack of photosynthesis (d) death of aquatic life.

A5. Which of the following oxides of nitrogen is not common air pollutant ?
(a) NO_2 (b) N_2O (c) NO (d) N_2O_5.

A6. White lung cancer is caused by
(a) asbestos (b) silica
(c) textiles (d) paper

A7. Which one of the following particulates is most toxic?
(a) fly ash (b) soot
(c) inorganic compound (d) smog.

A8. Besides CO_2, other greenhouse gas is
(a) CH_4 (b) N_2 (c) Ar (d) O_2.

A9. PAN stands for
(a) $CH_2 = O$ (b) $CH_2 = CH\ CH = O$
(c) $CH_3\ COONO_2$ (with O above the C) (d) $CH_3CH_2O - N = O$.

A10. Depletion of ozone layer causes
(a) blood cancer (b) breast cancer
(c) lung cancer (d) skin cancer

A11. Acid rains are produced by :
(a) excess release of carbon monoxide by incomplete combustion.
(b) excess formation of carbon dioxide by combustion and respiration.
(c) excess production of NH_3 by industries.
(d) excess NO_2 and SO_2 from burning fossil fuels.

A12. Oxides of sulphur and nitrogen are important pollutants of :
(a) Water (b) Air
(c) Soil (d) All of these.

A13. In upper stratosphere, ozone protects us from :
(a) infra-red radiations (b) ultra-violet radiations
(c) carbon dioxide (d) peroxyacetyl nitrate.

A14. Burning of fossil fuels is the main source of :
(a) Nitrogen dioxide (b) Nitric oxide
(c) Nitrous oxide (d) Sulphur dioxide.

A15. Which of the following gases is not a green house gas?
(a) CO (b) O_3
(c) CH_4 (d) H_2O vapour

A16. Taj Mahal is threatened by pollution from :
(a) Oxygen (b) Carbon dioxide
(c) Sulphur dioxide (d) Chlorine.

A17. Which of the following is the primary precursor of photochemical smog ?
(a) Ozone (b) Peroxyacetyl nitrate
(c) NO_2 (d) CO_2.

A18. The main contributor of acid rain is :
(a) H_2SO_4 (b) $CaCO_3$ (c) CH_3COOH (d) PAN.

A19. The main culprit for the depletion of protective ozone layer is :
(a) Oxygen (b) CFCs
(c) Oxides of S (d) Particulate matter.

A20. It is not advised to sleep in a closed room with a coke fire burning inside on a cold day because of harmful effects of :
(a) CO
(b) Carbon particulates
(c) CO_2
(d) SO_2 present as impurity in coke fire.

Answers

A1. (a) **A2.** (c) **A3.** (b) **A4.** (a) **A5.** (d) **A6.** (c) **A7.** (b) **A8.** (a) **A9.** (c) **A10.** (d)
A11. (d) **A12.** (b) **A13.** (b) **A14.** (d) **A15.** (a) **A16.** (c) **A17.** (c) **A18.** (a) **A19.** (b) **A20.** (a)

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A21. Bhopal Gas Tragedy was caused by :
(a) Methyl amine (b) Methyl isocyanate
(c) Phosgene (d) Chloroform.

A22. Which of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere ?
(a) Fullerenes (b) Freons
(c) Polyhalogens (d) Ferrocene.

A23. Most dangerous metal pollutant of automobile exhausts is
(a) Lead (b) Copper
(c) Mercury (d) Cadmium

A24. Which is most abundant hydrocarbon pollutant ?
(a) Methane (b) Propane
(c) Acetylene (d) Ethane.

Water Pollution

A25. Which of the following species containing mercury is most toxic ?
(a) CH_3Hg^+ (b) $HgCl_2$
(c) Hg_2Cl_2 (d) Hg metal.

A26. Which of the following metal has maximum recommended level in drinking water ?
(a) Cadmium (b) Zinc
(c) Aluminium (d) Iron.

A27. The clean water should have BOD value
(a) less than 5 ppm (b) 10 ppm
(c) 20 ppm (d) 100 ppm

A28. Which of the following has least permissible limit in drinking water ?
(a) Chlorides (b) Dissolved oxygen
(c) Zinc (d) Lead.

A29. COD stands for :
(a) Chemical Oxygen Demand.
(b) Controlled Oxygen Demand.
(c) Clouds causing Ozone Depletion.
(d) Chlorinated Oxygen Demand.

Soil Pollution

A30. Marble acts as a sink for
(a) metallic pollutants (b) NH_3 pollutants
(c) acidic pollutants (d) none of these.

A31. Herbicides are used to kill weeds. The common herbicide is
(a) D.D.T. (b) Triazine
(c) Methyl mercury (d) PCBS.

A32. Soil salinity can be measured by :
(a) Potentiometer (b) Calorimeter
(c) Conductivity meter (d) All of these.

A33. D.D.T. is :
(a) an antibiotic
(b) biodegradable pollutant
(c) non-degradable pollutant
(d) not a pollutant.

Answers

A21. (b) **A22.** (b) **A23.** (a) **A24.** (a) **A25.** (a) **A26.** (b) **A27.** (a) **A28.** (d) **A29.** (a) **A30.** (c) **A31.** (b) **A32.** (c) **A33.** (c)

B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

AIPMT & Other State Boards' Medical Entrance

B1. Ozone in the stratosphere is depleted by
(a) CF_2Cl_2 (b) C_7F_{16}
(c) $C_6H_6Cl_6$ (d) C_6F_6 *(A.I.I.M.S. 2004)*

B2. Which one of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere?
(a) polyhalogens (b) ferrocene
(c) fullerenes (d) freons *(CBSE P.M.T. 2004)*

B3. The environmental friendly method of killing harmful insects is through the use of
(a) Insecticides (b) Sex attractants
(c) Sex hormones (d) Pesticides
(e) Antibiotics *(Kerala PMT 2008)*

B4. The process of 'eutrophication' is due to
(a) Increase in concentration of insecticide in water
(b) Increase in concentration of fluoride ion in water
(c) The reduction in concentration of the dissolved oxygen in water due to phosphate pollution in water
(d) Attack of younger leaves of a plant by peroxyacetyl nitrate
(e) Increase in concentration of radioactive substances in water. *(Kerala PMT 2008)*

B5. Green chemistry means such reactions which :
(a) Produce colour during reactions
(b) Reduce the use and production of hazardous chemicals
(c) Are related to the depletion of ozone layer
(d) Study the reactions in plants. *(CBSE Med.2008)*

B6. Which one of the following statement is not true?
(a) pH of drinking water should be between 5.5-9.5
(b) Concentration of DO below 6 ppm is good for the growth of fish.
(c) Clean water would have a BOD value of less than 5 ppm.
(d) Oxides of sulphur, nitrogen and carbon, are the most widespread air pollutant. *(AIPMT 2011)*

B7. Excess nitrate in drinking water can cause
(a) methemoglobinemia
(b) liver damage (c) kidney damage
(d) laxative effect (e) leucoderma
(Kerala PMT 2011)

Answers

B1. (a) **B2.** (d) **B3.** (b) **B4.** (c) **B5.** (b) **B6.** (b) **B7.** (a)

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B8. Which of the following is not a greenhouse gas?
(a) Methane (b) Ozone
(c) Carbon dioxide (d) Nitrogen

B9. The pH of normal rain water is
(a) 6.5 (b) 7.5
(c) 5.6 (d) 3.5
(e) 4.6 *(Kerala PMT 2012)*

B10. Which one of the following statements regarding photochemical smog is not correct ?
(a) Carbon monoxide does not play any role in photochemical smog formation.
(b) Photochemical smog is an oxidising agent in character.
(c) Photochemical smog is formed through photochemical reaction involving solar energy.
(d) Photochemical smog does not cause irritation in eyes and throat. *(A.I.P.M.T. 2012)*

B11. Which one of the following is not a common component of photochemical smog?
(a) Ozone (b) Acrolein
(c) Peroxyacetyl nitrate (d) Chlorofluorocarbons
(AIPMT 2014)

B12. Which of the following is a sink for CO?
(a) Microorganisms present in the soil
(b) Oceans
(c) Plants
(d) Haemoglobin *(NEET 2017)*

B13. Which oxide of nitrogen is not a common pollutant introduced into the atmosphere both due to natural and human activity?
(a) N_2O_5 (b) NO_2
(c) N_2O (d) NO *(NEET 2018)*

JEE (Main) & Other State Boards' Engineering Entrance

B14. The smog is essentially caused by the presence of
(a) Oxides of sulphur and nitrogen
(b) O_2 and N_2
(c) O_2 and O_3
(d) O_3 and N_2 *(A.I.E.E.E.2004)*

B15. Identify the wrong statement in the following :
(a) Acid rain is mostly because of oxides of nitrogen and sulphur
(b) Chlorofluorocarbons are responsible for ozone layer depletion
(c) Greenhouse effect is responsible for global warming
(d) Ozone layer does not permit infrared radiation from the sun to reach the earth. *(AIEEE 2008)*

B16. The ozone layer forms naturally by
(a) the interaction of CFC with oxygen
(b) the interaction of UV radiation with oxygen
(c) the interaction of IR radiation with oxygen
(d) the interaction of oxygen and water vapour
(WB JEE 2011)

B17. The maximum prescribed concentration of cadmium in drinking water in ppm is
(a) 0.05 (b) 3
(c) 2 (d) 5
(e) 0.005 *(Kerala PET 2012)*

B18. The gas emitted by supersonic jet planes that slowly depletes the concentration of ozone layer is
(a) CO (b) NO
(c) SO_2 (d) O_2
(e) HF *(Kerala PET 2012)*

B19. CCl_4 and freons
(a) are green compounds because they are green coloured
(b) deplete ozone concentration
(c) cause increase in ozone concentration
(d) have no effect on ozone concentration
(J.K.C.E.T. 2012)

B20. What is D.D.T. among the following ?
(a) A fertilizer
(b) Biodegradable pollutant
(c) Non-biodegradable pollutant
(d) Greenhouse gas *(A.I.E.E.E. 2012)*

B21. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was
(a) Phosgene (b) Methylisocyanate
(c) Methylamine (d) Ammonia *(JEE Main 2013)*

B22. Metal ion responsible for the Minamata disease is
(a) Co^{2+} (b) Hg^{2+}
(c) Cu^{2+} (d) Zn^{2+} *(WB JEE 2014)*

B23. Among the following the one which is not a "greenhouse gas", is
(a) N_2O (b) CO_2
(c) CH_4 (d) O_2 *(WB JEE 2014)*

B24. Green chemistry deals with
(a) study of plant physiology
(b) study of extraction of natural products from plants
(c) detailed study of reactions involved in the synthesis of chlorophyll
(d) utilization of existing knowledge base for reducing the chemical hazards along with developmental activities
(e) synthesis of chemical compounds using green light.
(Kerala PET 2014)

B25. The wrong statement among the following is :
(a) Acid rain is mostly because of oxides of nitrogen and sulphur.
(b) Greenhouse effect is responsible for global warming.
(c) Ozone layer does not permit infrared radiation from the sun to reach earth.
(d) Chlorofluorocarbons are responsible for ozone layer depletion. *(J.K. CET 2015)*

Answers

B8. (d) **B9.** (c) **B10.** (d) **B11.** (d) **B12.** (a) **B13.** (a) **B14.** (a) **B15.** (d) **B16.** (b) **B17.** (e) **B18.** (b)
B19. (b) **B20.** (c) **B21.** (b) **B22.** (b) **B23.** (d) **B24.** (d) **B25.** (c)

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B26. The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 100 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of :
(*a*) Fluoride (*b*) Lead
(*c*) Nitrate (*d*) Iron (*JEE Main 2016*)

B27. Which one of the following is not a common component of photochemical smog?
(*a*) Ozone (*b*) Acrolein
(*c*) Peroxyacetylnitrate (*d*) Chlorofluorocarbons (*Karnataka CET 2017*)

B28. A water sample has ppm level co ncentration of following anions
$F^- = 10$; $SO_4^{2-} = 100$; $NO_3^- = 50$
the anion/anions that make/makes the water sample unsuitable for drinking is/are:
(*a*) only NO_3^- (*b*) both SO_4^{2-} and NO_3^-
(*c*) only F^- (*d*) only SO_4^{2-} (*JEE Main 2017*)

B29. Green fuel is the fuel obtained from
(*a*) bio-waste (*b*) metal waste
(*c*) plastic waste (*d*) chemical waste
(*e*) electronic waste. (*Kerala PET 2018*)

B30. Which of the following is present in maximum amount in acid rain?
(*a*) HNO_3 (*b*) H_2SO_4
(*c*) HCl (*d*) H_2CO_3 (*WB JEE 2018*)

B31. The recommended concentration of fluoride ion in drinking water is up to 1 ppm as fluoride ion is required to make teeth enamel harder by converting $[3Ca_3(PO_4)_2.\ Ca(OH)_2]$ to :
(*a*) $[CaF_2]$ (*b*) $[3(CaF_2).Ca(OH)_2]$
(*c*) $[3Ca_3(PO_4)_2.CaF_2]$ (*d*) $[3\{Ca(OH)_2\}.CaF_2]$ (*JEE Main 2018*)

B32. The molecule that has minimum/no role in the formation of photochemical smog, is
(*a*) NO (*b*) $CH_2{=}O$
(*c*) O_3 (*d*) N_2 (*JEE Main 2019*)

B33. Water samples with BOD values of 4 ppm and 18 ppm respectively, are
(*a*) Clean and highly polluted
(*b*) Clean and clean
(*c*) Highly polluted and clean
(*d*) Highly polluted and highly polluted (*JEE Main 2019*)

Answers

B26. (*c*) **B27.** (*d*) **B28.** (*c*) **B29.** (*a*) **B30.** (*b*) **B31.** (*c*) **B32.** (*d*) **B33.** (*a*)

C MULTIPLE CHOICE QUESTIONS *with more than one correct answer*

C1. The gases causing greehouse effect is/are
(*a*) CH_4 (*b*) NO_2 (*c*) SO_2 (*d*) O_3

C2. Which of the following conditions show the polluted environment?
(*a*) pH of rain water in 5.6.
(*b*) eutrophication.
(*c*) biochemical oxygen demand 10 ppm.
(*d*) amount of carbon dioxide in the atmosphere is 0.03%

C3. The acids present in acid rain are
(*a*) H_2CO_3 (b) Peroxyacetylnitrate
(*c*) H_2SO_4 (*d*) HNO_3

C4. The atmosphere surrounding us may be divided into the following regions.
(*a*) mesosphere (*b*) hemisphere
(*c*) thermosphere (*d*) catosphere

C5. The ozone layer is depleted by
(*a*) SO_2 (*b*) C_xH_y (*c*) NO (*d*) CFCs

Answers

C1. (*a, d*) **C2.** (*b,c*) **C3.** (*a,c,d*) **C4.** (*a,c*) **C5.** (*c,d*)

Assertion Reason Type Questions

The questions given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
(*c*) If assertion is CORRECT, but reason is INCORRECT.
(*d*) If assertion is INCORRECT, but reason is CORRECT.
(*e*) If both asseriton and reason are INCORRECT.

1. Assertion : Photochemical smog is produced by oxides of nitrogen.
Reason : Vehicular pollution is a major source of oxides of nitrogen.

2. Assertion : For greenhouse effect, presence of green plants is essential.
Reason : Chlorophyll of the green plants causes green house effect.

3. Assertion : Normal rain water has a pH of about 5.6.
Reason : The pH is due to dissolution of CO_2 to form carbonic acid.

4. Assertion : In India, an oil spill occurred in Bombay in 1993.
Reason : Spreading of oil into sea is called oil spill.

Answers

1. (*b*) **2.** (*e*) **3.** (*a*) **4.** (*b*)

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5. Assertion : Higher concentration of CO_2 in atmosphere is causing global warming.
Reason : This is due to greenhouse effect.

6. Assertion : The presence of CO reduces the amount of haemoglobin available in the blood for carrying oxygen to the body cells.
Reason : CO combines with haemoglobin about 200 times less easily than oxygen to form complex.

7. Assertion : Photochemical smog is oxidising in nature.
Reason : Photochemical smog contains NO_2 and O_3, which are formed during the sequences of reactions.

8. Assertion : Ozone is destroyed by solar radiation in upper stratosphere.
Reason : Depletion of the ozone layer allows excessive UV radiations to reach the surface of earth.
(NCERT Exemplar Problem)

9. Assertion : Excessive use of chlorinated synthetic pesticides causes soil and water pollution.
Reason : These pesticides are non-biodegradable.
(NCERT Exemplar Problem)

10. Assertion : The pH of acid rain is less than 5.6.
Reason : Carbon dioxide present in the atmosphere dissolves in rain water and forms carbonic acid. *(NCERT Exemplar Problem)*

11. Assertion : If BOD level of water in a reservoir is less than 5 ppm it is highly polluted.
Reason : High BOD means low activity of bacteria in water. *(NCERT Exemplar Problem)*

12. Assertion : Green house effect was observed in houses made of green glass which are used to grow plants.
Reason : Green house name has been given because glass houses are made of green glass. *(NCERT Exemplar Problem)*

Answers

5.(*a*) **6.** (*c*) **7.** (*a*) **8.** (*d*) **9.**(*a*) **10.** (*b*) **11.** (*e*) **12.** (*e*)

NCERT Exemplar Problems
Objective Questions

Multiple Choice Questions (Type-I)

1. Which of the following gases is not a green house gas?
(*a*) CO (*b*) O_3
(*c*) CH_4 (*d*) H_2O vapour

2. Photochemical smog occurs in warm, dry and sunny climate. One of the following is not amongst the components of photochemical smog, identify it.
(*a*) NO_2 (*b*) O_3
(*c*) SO_2 (*d*) Unsaturated hydrocarbon

3. Which of the following statement is **not** true about classical smog?
(*a*) Its main components are produced by the action of sunlight on emissions of automobiles and factories.
(*b*) Produced in cold and humid climate.
(*c*) It contains compounds of reducing nature.
(*d*) It contains smoke, fog and sulphur dioxide.

4. Biochemical Oxygen Demand, (BOD) is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to be ____ .
(*a*) rich in dissolved oxygen
(*b*) poor in dissolved oxygen.
(*c*) highly polluted.
(*d*) not suitable for aquatic life

5. Which of the following statements is wrong?
(*a*) Ozone is not responsible for green house effect.
(*b*) Ozone can oxidise sulphur dioxide present in the atmosphere to sulphur trioxide.
(*c*) Ozone hole is thinning of ozone layer present in stratosphere.
(*d*) Ozone is produced in upper stratosphere by the action of UV rays on oxygen.

6. Sewage containing organic waste should be disposed in water bodies because it causes major water pollution. Fishes in such a polluted water die because of
(*a*) Large number of mosquitoes.
(*b*) Increase in the amount of dissolved oxygen.
(*c*) Decrease in the amount of dissolved oxygen in water.
(*d*) Clogging of gills by mud.

7. Which of the following statements about photochemical smog is wrong?
(*a*) It has high concentration of oxidising agents.
(*b*) It has low concentration of oxidising agents.
(*c*) It can be controlled by controlling the release of NO_2, hydrocarbons, ozone etc.
(*d*) Plantation of some plants like pinus helps in controlling photochemical smog.

8. The gaseous envelope around the earth is known as atmosphere. The lowest layer of this is extended upto 10 km from sea level, this layer is _____ .
(*a*) Stratosphere (*b*) Troposphere
(*c*) Mesosphere (*d*) Hydrosphere

Answers

1. (*a*) **2.** (*c*) **3.** (*a*) **4.** (*a*) **5.** (*a*) **6.** (*c*) **7.** (*b*) **8.** (*b*)

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9. Dinitrogen and dioxygen are main constituents of air but these do not react with each other to form oxides of nitrogen because _____ .
(*a*) the reaction is endothermic and requires very high temperature.
(*b*) the reaction can be initiated only in presence of a catalyst.
(*c*) oxides of nitrogen are unstable.
(*d*) N_2 and O_2 are unreactive.

10. The pollutants which come directly in the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants?
(*a*) CO (*b*) Hydrocarbon
(*c*) NO (*d*) Peroxyacetyl nitrate

11. Which of the following statements is correct?
(*a*) Ozone hole is a hole formed in stratosphere from which ozone oozes out.
(*b*) Ozone hole is a hole formed in the troposphere from which ozone oozes out.
(*c*) Ozone hole is thinning of ozone layer of stratosphere at some places.
(*d*) Ozone hole means vanishing of ozone layer around the earth completely.

12. Which of the following practices will **not** come under green chemistry?
(*a*) If possible, making use of soap made of vegetable oils instead of using synthetic detergents.
(*b*) Using H_2O_2 for bleaching purpose instead of using chlorine based bleaching agents.
(*c*) Using bicycle for travelling small distances instead of using petrol/diesel based vehicles.
(*d*) Using plastic cans for neatly storing substances.

Answers

9. (*a*) **10.** (*d*) **11.** (*c*) **12.** (*d*)

Multiple Choice Questions (Type-II)

13. Which of the following conditions shows the polluted environment.
(*a*) pH of rain water is 5.6.
(*b*) amount of carbon dioxide in the atmosphere is 0.03%.
(*c*) biochemical oxygen demand 10 ppm.
(*d*) eutrophication.

14. Phosphate containing fertilisers cause water pollution. Addition of such compounds in water bodies causes ____ .
(*a*) enhanced growth of algae.
(*b*) decrease in amount of dissolved oxygen in water.
(*c*) deposition of calcium phosphate.
(*d*) increase in fish population.

15. The acids present in acid rain are _____ .
(*a*) Peroxyacetyl nitrate (*b*) H_2CO_3
(*c*) HNO_3 (*d*) H_2SO_4

16. The consequences of global warming may be ____ .
(*a*) increase in average temperature of the earth.
(*b*) melting of Himalayan Glaciers.
(*c*) increased biochemical oxygen demand.
(*d*) eutrophication.

Matching Type Questions

In the following questions more than one option of Column I and Column II may match.

17. Match the terms given in Column I with the compounds given in Column II.

Column I	*Column II*
(*i*) Acid rain	(*a*) $CHCl_2 - CHF_2$
(*ii*) Photochemical smog	(*b*) CO
(*iii*) Combination with haemoglobin	(*c*) CO_2
(*iv*) Depletion of ozone layer	(*d*) SO_2
	(*e*) Unsaturated hydrocarbons

18. Match the pollutant(s) in Column I with the effect(s) in Column II.

Column I	*Column II*
(*i*) Oxides of sulphur	(*a*) Global warming
(*ii*) Nitrogen dioxide	(*b*) Damage to kidney
(*iii*) Carbon dioxide	(*c*) 'Blue baby' syndrome
(*iv*) Nitrate in drinking water	(*d*) Respiratory diseases
(*v*) Lead	(*e*) Red haze in traffc and congested areas

Answers

13. (*c, d*) **14.** (*a, b*) **15.** (*b, c, d*) **16.** (*a, b*) **17.** (*i*) – (*c, d*); (*ii*) – (*e, d*); (*iii*) – (*b*); (*iv*) – (*a*)
18. (*i*) – (*d*); (*ii*) – (*e*); (*iii*) – (*a*); (*iv*) – (*c*), (*v*) – (*b*)

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19. Match the activity given in Column I with the type of pollution created by it given in Column II.

Column I (Activity)	*Column II* (Effect)
(*i*) Releasing gases to the atmosphere after burning waste material containing sulphur.	(*a*) Water pollution
(*ii*) Using carbamates as pesticides	(*b*) Photochemical smog, damage to plant life, corrosion to building material, induce breathing problems, water pollution
(*iii*) Using synthetic detergents for washing clothes	(*c*) Damaging ozone layer
(*iv*) Releasing gases produced by automobiles and factories in the atmosphere.	(*d*) May cause nerve diseases in human.
(*v*) Using chlorofluorocarbon compounds for cleaning computer parts	(*e*) Classical smog, acid rain, water pollution, induce breathing problems, damage to buildings, corrosion of metals.

20. Match the pollutants given in Column I with their effects given in Column II.

Column I	*Column II*
(*i*) Phosphate fertilisers in water	(*a*) BOD level of water increases
(*ii*) Methane in air	(*b*) Acid rain
(*iii*) Synthetic detergents in water	(*c*) Global warming
(*iv*) Nitrogen oxides in air	(*d*) Eutrophication

Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

(*a*) Both A and R are correct and R is the correct explanation of A.
(*b*) Both A and R are correct but R is not the correct explanation of A.
(*c*) Both A and R are not correct.
(*d*) A is not correct but R is correct.

21. Assertion (A) : Green house effect was observed in houses used to grow plants and these are made of green glass.
Reason (R) : Green house name has been given because glass houses are made of green glass.

22. Assertion (A) : The pH of acid rain is less than 5.6.
Reason (R) : Carbon dioxide present in the atmosphere dissolves in rain water and forms carbonic acid.

23. Assertion (A) : Photochemical smog is oxidising in nature.
Reason (R) : Photochemical smog contains NO_2 and O_3, which are formed during the sequence of reactions.

24. Assertion (A) : Carbon dioxide is one of the important greenhouse gases.
Reason (R) : It is largely produced by respiratory function of animals and plants.

25. Assertion (A) : Ozone is destroyed by solar radiation in upper stratosphere.
Reason (R) : Thinning of the ozone layer allows excessive UV radiations to reach the surface of earth.

26. Assertion (A) : Excessive use of chlorinated synthetic pesticides causes soil and water pollution.
Reason (R) : Such pesticides are non-biodegradable.

27. Assertion (A) : If BOD level of water in a reservoir is less than 5 ppm it is highly polluted.
Reason (R) : High biological oxygen demand means low activity of bacteria in water.

Answers

19. (*i*) – (*e*); (*ii*) – (*d*); (*iii*) – (*a*); (*iv*) – (*b*); (*v*) – (*c*) **20.** (*i*) – (*a, d*); (*ii*) – (*c*); (*iii*) – (*a*); (*iv*) – (*b*) **21.** (*c*) **22.** (*b*) **23.** (*a*) **24.** (*b*) **25.** (*d*) **26.** (*a*) **27.** (*c*)

Hints & Explanations for *Difficult Objective Type Questions*

B1. (*a*) : Ozone is depleted by chlorofluorocarbons (CF_2Cl_2).

B2. (*d*) : Chlorofluorocarbons known as freons deplete ozone layer.

B6.(*b*) : Fish dies in water bodies polluted by sewage or other pollutants due to decrease in dissolved oxygen (D.O.) value below 6 ppm.

B7.(*a*) : Excess nitrate in drinking water can cause methemoglobinemia (blue baby syndrome).

B8. (*d*) : Nitrogen is not a greenhouse gas.

B11. (*d*) : Chlorofluorocarbons are not a common component of photochemical smong.

B12. (*a*) : Microorganisms present in the soil is the sink of CO.

B13. (*a*) : N_2O_5 is not a common pollutant.

B16. (*b*) : Ozone layer is formed in the atmosphere by the decomposition of oxgen by ultra-violet radiation.

B20. (*c*) : D.D.T. is non-biodegradable pollutant.

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Competition File

B21. (b) : The gas leaked in Bhopal gas tragedy was methylisocyanate ($CH_3N = C = O$).

B23. (d) : O_2 is not a greenhouse gas.

B26. (c) : The permissible limit of nitrate in water is about 50 ppm. Hence the concentration of NO_3^- ions in a given water sample exceeds from the permissible limit. The higher concentration of NO_3^- ions in water may cause blue baby syndrome disease.

B28. (c) : The F^- ion concentration is above the permissible limit in drinking water. Therefore, it is unsuitable for drinking. Excess concentration of F^- ions (greater than 2 ppm) causes brown mottling of teeth enamel.

B31. (c) : F^- ions make the teeth enamel harder by converting

$3Ca_3(PO_4)_2.Ca(OH)_2 \longrightarrow 3Ca_3(PO_4)_2.CaF_2$

B32. (d) : NO, O_3 and HCHO are involved in the formation of photochemical smog. N_2 has no role in photochemical smog.

B33. (a) : Clean water would have BOD value < 5ppm while BOD value of > 17 indicates highly polluted water.

NCERT Exemplar Problems : MCQs Type-I

3. (a) : Classical smog is not produced by the action of sunlight on emissions of automobiles and factories.

5. (a) : Ozone is also one of the greenhouse gas.

6. (c) : Organic waste consumes oxygen and therefore, dissolved oxygen in water decreases and fish in such polluted water die.

7. (b) : Photochemical smog is oxidising in nature because it contains large concentration of oxidising agents such as O_3 and NO_2.

10. (d) : Peroxyacetyl nitrate is a secondary pollutant which is formed from primary pollutants such as NO_2, O_3 and hydrocarbons.

NCERT Exemplar Problems : MCQs Type-II

15. (b, c, d) : The acids present in acid rain are H_2CO_3, HNO_3 and H_2SO_4.

16. (a, b) : The global warming may result into increase in average temperature of the earth and melting of Himalayan glaciers.

Unit Practice Test

for Board Examination

Time Allowed: 1 Hr. ***Maximum Marks: 25***

1.	Fish do not grow as well in warm water as in cold water. Why?	(1)
2.	What do the abbreviations 'BOD' and 'COD' stand for ?	(1)
3.	What are herbicides? Give one example.	(1)
4.	What is the major cause of ozone layer destruction?	(1)
5.	Name the gas which caused Bhopal gas tragedy?	(1)
6.	What is pneumoconiosis? How does it occur?	(2)
7.	Why does rain water normally have a pH of about 5.6 ? When does it become acidic rain?	(2)
8.	How can domestic waste be used as manure?	(2)
9.	Statues and monuments in India are affected by acid rain. How?	(2)
10.	List main differences between classical smog and photochemical smog.	(3)
11.	Give a brief account of green chemistry.	(3)
12.	Explain (*i*) Green house effect (*ii*) Tropospheric pollution.	(3)
13.	What are the reactions involved in ozone layer depletion in stratosphere ? What are its consequences ?	(3)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part II of the book.

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According to Completely CBSE Pattern

MOCK TEST – 2

Time allowed : 3 hours ***Maximum Marks : 70***

General Instructions :

(*i*) *All questions are compulsory.*
(*ii*) *Question nos. 1 to 5 are very short answer questions and carry 1 mark each.*
(*iii*) *Question nos. 6 to 12 are short answer questions and carry 2 marks each.*
(*iv*) *Question 13 to 24 are also short answer questions and carry 3 marks each.*
(*v*) *Question nos. 25 to 27 are long answer questions and carry 5 marks each.*
(*vi*) *Use log tables if necessary. Use of calculators in not allowed.*

Chapters Included :

8. Redox Reactions
9. Hydrogen
10. *s*-Block Elements (Alkali and Alkaline Earth Metals)
11. Some p-Block Elements
12. Organic Chemistry : Some Basic Principles and Techniques
13. Hydrocarbons
14. Environmental Pollution

1. Name the compound formed by the oxidation of ethyl benzene by $KMnO_4$. (1)

2. Which of the following is acidic?

(*i*) But-1-yne (*ii*) But-2-yne (*iii*) But-1-ene (*iv*) But-2-ene (1)

3. Compare the behaviour of CCl_4 and BCl_3 with water. (1)

4. Which out of lithium or sodium forms nitrides? (1)

5. Name a compound which retards the decomposition of H_2O_2. (1)

6. Give two examples each of ionic hydrides and covalent hydrides. (2)

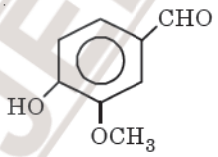
7. Why is Li_2CO_3 decomposed at a lower temperature while Na_2CO_3 is decomposed at higher temperature? (2)

8. Explain the higher stability of BCl_3 as compared to $TlCl_3$. (2)

9. Give condensed and bond line structural formulae for the following :

(*i*) 2-(4-isobutylphenyl) propanoic acid (*ii*) Hexanedial (2)

10. Write the IUPAC names of the following compounds :

(*i*) $(CH_3)_2C(C_2H_5)_2$ (*ii*) 

(2)

11. What is acid rain? What are its harmful effects? (2)

12. What is salt bridge? Give its functions. (2)

13. 0.35 g of an organic substance was Kjeldahlised and ammonia obtained was passed into 100 mL of $\frac{N}{10}H_2SO_4$. The excess acid required 154 mL of $\frac{N}{10}$ NaOH for neutralisation. Calculate the percentage of nitrogen in the compound. (3)

14. Give one method of preparation of each of the following :

(*i*) Ethane
(*ii*) Propyne
(*iii*) Ethene (3)

15. Write short notes on the following :

(*a*) Wurtz reaction
(*b*) Markovnikov's rule
(*c*) Friedel Craft reaction (3)

16. What do you mean by green chemistry? How will it help decrease environmental pollution? (3)

17. Give the chemistry of Lassaigne's test for nitrogen and halogens. (3)

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18. Complete the following reactions :

(*i*) $CH_3—C\equiv C—Ph \xrightarrow{Hg^{2+},\ H^+}$ (*ii*) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=CH_2 \xrightarrow{Br_2,\ H_2O}$

(*iii*) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=CHCH_3 \xrightarrow[Zn,H_2O]{O_3,}$ (3)

19. Write the structures and IUPAC names of different structural isomers of alkenes corresponding to the formula C_5H_{10}. (3)

20. Explain the following reactions :

(*i*) CO is heated with ZnO.

(*ii*) Hydrated alumina is heated with aqueous NaOH.

(*iii*) Silicon is heated with methyl chloride at high temperature in the presence of copper. (3)

21. Explain the following :

(*a*) Boric acid is polymeric

(*b*) Lead (IV) chloride is highly unstable towards heat.

(*c*) Graphite is used as a lubricant. (3)

22. (*a*) Why do alkenes under go electrophilic addition reactions? Give one example.

(*b*) An organic compound 'X' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'X'. (3)

23. (*a*) What is meant by disproportionation reaction? Give one example.

(*b*) Balance the following redox reactions :

(*i*) $Br_2 + H_2O_2 \longrightarrow BrO_3^- + H_2O$ (acidic medium)

(*ii*) $P(s) + OH^-(aq) \longrightarrow PH_3(g) + H_2PO_2^-(aq)$ (3)

24. (*a*) Write down the chemical reactions involved during the formation of photochemical smog.

(*b*) Which out of CO or CO_2 is more dangerous pollutant? (3)

25. (*a*) What is diagonal relationship? How does lithium resemble magnesium?

(*b*) Explain the structure of diborane.

(*c*) Give three important uses of aluminium.

(*d*) $N(CH_3)_3$ is pyramidal but $N(SiH_3)_3$ is planar. Explain.

(*e*) Like CO why its analogue SiO is not stable. (5)

Or

(*a*) What are fullerenes? Discuss their structures.

(*b*) What are silicones? How are they prepared? Give their important uses.

26. (*a*) Describe Carius method for the estimation of halogens.

(*b*) What is the difference between distillation and fractional distillation.

(*c*) What is the structure of a carbanion? Explain the stability of CH_3^-, 1°, 2° and 3° carbanions. (5)

Or

Give a brief account of the following;

(*i*) hyperconjugation (*ii*) inductive effect (*iii*) electromeric effect

27. (*a*) Account for the acidity of alkynes.

(*b*) Explain the mechanism of sulphonation of benzene.

(*c*) How will you convert the following :

(*i*) Ethyne to but-2-yne (*ii*) Propene to 2, 3-dimethylbutane (*iii*) Ethene to ethyne. (5)

Or

(*a*) Explain the orbital picture of benzene.

(*b*) Give three methods of preparation of benzene.

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According to Completely CBSE Pattern

MOCK TEST – 3

Time allowed : 3 hours *Maximum Marks : 70*

General Instructions :

(*i*) *All questions are compulsory.*
(*ii*) *Question nos. 1 to 5 are very short answer questions and carry 1 mark each.*
(*iii*) *Question nos. 6 to 12 are short answer questions and carry 2 marks each.*
(*iv*) *Question 13 to 24 are also short answer questions and carry 3 marks each.*
(*v*) *Question nos. 25 to 27 are long answer questions and carry 5 marks each.*
(*vi*) *Use log tables if necessary. Use of calculators in not allowed.*

COMPLETE SYLLABUS

1. An aqueous solution of sodium carbonate gives alkaline tests. Why? (1)

2. What is the oxidation state of S in $Na_2S_2O_3$? (1)

3. What will be the pH of a 0.1 M ammonium acetate if $pK_a = pK_b = 4.74$? (1)

4. Write the conjugate acids of C_6H_5OH and NH_2NH_2. (1)

5. The equilibrium constant of a reaction at 27°C and 127° C are 1.52×10^{-4} and 1.26×10^{-2} respectively. Is the reaction exothermic or endothermic? (1)

6. Give molecular electronic configuration of peroxide ion and oxygen molecule. Which of the two has larger bond length? (2)

7. How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium? (2)

8. Calculate the wavelength of an electron having mass = 9.1×10^{-31} kg and kinetic energy = 3.0×10^{25} J. (2)

9. If 20.0 g of $CaCO_3$ is treated with 20.0 g of HCl, how many grams of CO_2 can be produced according to the reaction :

$$CaCO_3(s) + 2HCl\,(aq) \longrightarrow CaCl_2\,(aq) + H_2O(l) + CO_2(g)$$ (2)

10. For the water gas reaction :

$$C(s) + H_2O\,(g) \longrightarrow CO(g) + H_2(g)$$

the standard Gibbs energy for the reaction at 1000K is –8.1 kJ mol^{-1}. Calculate its equilibrium constant. (2)

11. What is the relation between kinetic energy and temperature? (2)

12. Describe the shapes of BF_3 and BH_4^- and assign the hybridisation of boron in these species. (2)

13. Draw structures of cyclic and acylic isomers of molecular formula C_3H_6O. (3)

14. (*a*) Which of the two : $O_2N\,CH_2\,CH_2O^-$ or $CH_3\,CH_2O^-$ is expected to be more stable and why?

(*b*) Why alkyl groups act as electron donors when attached to a π-system.

(*c*) Which of the following carbocation is more stable :

(*i*) $(CH_3)_3CCH_2^+$ (*ii*) $CH_3\overset{+}{C}HCH_2CH_3$ (*iii*) $CH_3CH_2CH_2^+$ (3)

15. How will you convert :

(*i*) Ethane to butane (*ii*) Ethane to ethyne (*iii*) Ethyne to methane (3)

16. (*a*) Write down the products of ozonolysis of 1, 2-dimethylbenzene (o-xylene). How do the results support the Kekule structure of benzene?

(*b*) Why is benzene extra ordinarily stable though it contains three double bonds? (3)

17. Give the reasons :

(*i*) Aluminium wires are used to make transmission cables.

(*ii*) Diamond is used as an abrasive.

(*iii*) Aluminium utensils should not be kept in water overnight. (3)

18. Complete the following reactions :

(*i*) $Ca_3N_2(s) + H_2O(l) \longrightarrow$ (*ii*) $MnO_4^- + H^+ + H_2O_2 \longrightarrow$ (*iii*) $I_2 + H_2O_2 + OH^- \longrightarrow$ (3)

19. (*a*) The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2, and H^+ ion. Write a balanced ionic equation for the reaction.

(*b*) Predict the product of electrolysis of an aqueous solution of $AgNO_3$ with Ag electrodes. (3)

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20. (*a*) The wavelength of first spectral line in the Balmer series is 6561 Å. Calculate the wavelength of the second spectral line in Balmer series.

(*b*) How many electrons in a given atom can have the following quantum number values :

$n = 4, l = 2, m = \pm 1$ (3)

21. Commercially available sulphuric acid contains 93% acid by mass and has a density of 1.84 g mL^{-1}. Calculate (*i*) the molarity of the solution (*ii*) volume of concentrated acid required to prepare 2.5 L of 0.50 M H_2SO_4. (3)

22. (*a*) Define the following

(*i*) enthalpy of combustion (*ii*) enthalpy of formation

(*b*) The enthalpy change for the reaction :

$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

is 92.2 kJ. What is the enthalpy of formation of ammonia? (3)

23. (*a*) Name two phenomena which can be explained as the basis of surface tension.

(*b*) What is compressibility factor? How does it help to account for the nature of the gas? (3)

24. (*a*) Calculate the strength in volumes of a solution containing 30.36 g/L of H_2O_2.

(*b*) Complete the following reactions:

(*i*) $CaOCl_2 + H_2O_2 \longrightarrow$ (*ii*) $Fe_2(SO_4)_3 + H_2O_2 + NaOH \longrightarrow$ (3)

25. (*a*) On the basis of VSEPR theory, explain the shapes of following :

H_2O and NH_3 molecules.

(*b*) Draw resonance structures for SO_3 and CO_2 molecules.

(*c*) Which out of NH_3 and NF_3 has higher dipole moment and why ? (5)

Or

(*a*) Explain the structures of the following molecules on the basis of hybridisation.

(*i*) PF_5 (*ii*) BrF_5 (*iii*) XeF_4

(*b*) Ice floats over water. Explain.

(*c*) Out of MgO and LiCl, which has higher lattice enthalpy?

26. (*a*) What is solubility product? How is it different from ionic product.

(*b*) Calculate the molar solubility of $Ni(OH)_2$ in 0.10 M NaOH.

K_{sp} of $Ni(OH)_2 = 2.0 \times 10^{-15}$.

(*c*) What are acidic buffers? Give one example.

(*d*) Calculate the pH of 10^{-8} M HCl solution. (5)

Or

(*a*) How will you show that in a reversible reaction, equilibrium can be achieved from either direction?

(*b*) What is Le Chatelier's principle. With the help of this explain : ice melts when pressure is applied on it.

(*c*) Calculate the pH of a solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4.

27. (*a*) Assign structures for the following :

(*i*) An alkyne (X) has molecular formula C_5H_8. It reacts neither with sodamide nor with ammoniacal cuprous chloride.

(*ii*) A hydrocarbon 'Y' decolourises bromine water. On ozonolysis it gives 3-methyl butanal and formaldehyde. Give the name of the compound.

(*iii*) A hydrocarbon (Z) has molecular formula C_8H_{10}. It does not decolourise bromine water and is oxidised to benzoic acid on heating with $K_2Cr_2O_7$. It can also have three other isomers A, B and C. Write the structures of Z, A, B and C.

(*b*) What effect does branching of an alkane chain has on its boiling point?

(*c*) Draw *cis* and *trans* isomers of hex-2-ene. Which isomer will have higher boiling point? (5)

Or

(*a*) Give the basic difference between Duma's method and Kjeldahl's method for the estimation of nitrogen.

(*b*) How will you convert:

(*i*) Acetylene to but-1-yne (*ii*) Propene to propan-1-ol (*iii*) ethanoic acid to ethane

(*c*) Suggest a suitable technique for the separation of naphthalene from kerosene present in a mixture.

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Solution File

Hints & Solutions for *Unit Practice Tests & Mock Tests*

UNIT PRACTICE TEST–8

1. +6 because there is one peroxide bond (–O–O–) *i.e.*, O_2^{2-}
2. Oxidising agent : Cu^{2+}, reducing agent : I^-.
3. Na_2O_2 (–1), OF_2(+2)
4. The reaction in which an element in one oxidation state is simultaneously oxidised and reduced.
5. No, because the oxidation number of Cr has neither increased nor decreased but remains +6.
6. Since reduction potential of silver is more than that of hydrogen ($E°_{H^+|H_2}$, Pt = 0), silver vessel will be suitable to store 1M HCl. On ther other hand, $E°_{Al^{3+}|Al}$ is less than that of hydrogen ($E°_{H^+|H_2}$, Pt) so that hydrogen will be liberated if stored in aluminium vessel.
7. (*i*) $\overset{+3}{Fe_2}\overset{-2}{O_3} + 3\overset{+2}{C}\overset{-2}{O} \longrightarrow 2\overset{0}{Fe}(s) + 3\overset{+4}{C}\overset{-2}{O_2}$

   O.N. of Fe decreases from +3 (in Fe_2O_3) to 0 (in Fe) and that of C increases from +2 (in CO) to +4 (in CO_2). Therefore, Fe_2O_3 is reduced while CO is oxidised. Thus, this is a redox reaction.

   (*ii*) $4\overset{-3}{N}\overset{+1}{H_3}(g) + 5\overset{0}{O_2}(g) \longrightarrow 4\overset{+2}{N}\overset{-2}{O}(g) + 6\overset{+1}{H_2}\overset{-2}{O}(g)$

   In this case O.N. of N increases from –3 (in NH_3) to +2 (in NO) and that of O decreases from 0 (in O_2) to –2 (in H_2O). Therefore, NH_3 has been oxidised while O_2 has been reduced. Hence, it is a redox reaction.
8. In AgF_2, oxidation state of Ag is +2 which is very unstable. Therefore, it readily accepts an electron to form a more stable oxidation state of +1 as

   $$Ag^{2+} + e^- \longrightarrow Ag^+$$

   Therefore, AgF_2 if formed will act as a strong oxidising agent.
9. The O.S. of S in $S_2O_3^{2-}$ is +2, in $S_4O_6^{2-}$ it is +2.5 (average) and in SO_4^{2-} it is +6. Since Br_2 is a stronger oxidising agent than I_2, it oxidises S of $S_2O_3^{2-}$ to SO_4^{2-} (with higher O.S. of +6). However, I_2 being a weaker oxidising agent, it oxidises S of $S_2O_3^{2-}$ into a lower O.S. of +2.5 in $S_4O_6^{2-}$. Therefore, $S_2O_3^{2-}$ reacts differently with Br_2 and I_2.
10. The cell may be depicted similar to Fig. 3. It may be represented as :

    $$Zn(s) \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag$$

    (*i*) Zinc electrode (anode)

    (*ii*) At anode : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

    At cathode : $Ag^+(aq) + e^- \longrightarrow Ag(s)$
11. *Refer Solved Example 30*
12. *Refer Solved Example 20 (ii) and (iv).*
13. *Refer Solved NCERT Exercise, Q.4 and 5.*

UNIT PRACTICE TEST–9

1. Perhydrol
2. Conc. H_2SO_4 on absorbing water from moist H_2 produces so much heat that H_2 catches fire.
3. Deuteroacetylene is formed :

   $$CaC_2 + D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$
4. 1 : 2 : 3
5. Heavy water is injurious to plants, animals and human beings because it slows down the rates of reactions occurring in them. So, it cannot be used.
6. *Refer NCERT File Q. 24.*
8. $2H_2O_2 \longrightarrow 2H_2O + O_2$

   68 g 22.4L at N.T.P.

   22.4L of O_2 at N.T.P. is produced from H_2O_2 = 68 g

   25 L of O_2 at N.T.P. is produced from H_2O_2

   $$= \frac{68}{22.4} \times 25 = 75.9 \text{ g}$$

   Strength of 25 volume H_2O_2 = 75.9 g/L

   Amount of H_2O_2 present in 10 mL = $\frac{75.9}{1000} \times 10$

   = 0.759 g.
9. *Refer NCERT File Q. 7.*
10. *Refer NCERT File Q. 8.*
11. (*a*) $Zn(s) + 2NaOH(aq) \longrightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2(aq)} + H_2(g)$

    (*b*) $4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3\,HCl$

    (*c*) $Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$

UNIT PRACTICE TEST–10

1. Francium and radium
2. Both Li^+ and H^- have small size and their combination has high lattice energy. Therefore, LiH is stable as compared to NaH.
3. Lithium
4. C_6H_6
5. +1
6. Potassium carbonate cannot be prepared by Solvay process because potassium bicarbonate being more soluble than sodium bicarbonate does not get precipitated when CO_2 is passed through a concentrated solution of KCl saturated with NH_3.
7. Beryllium and magnesium atoms in comparison to other alkaline earth metals are comparatively smaller and their ionisation enthalpies are very high. Hence,

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Solution File

the energy of the flame is not sufficient to excite their electrons to higher energy levels. These elements, therefore, do not give any colour in Bunsen flame.

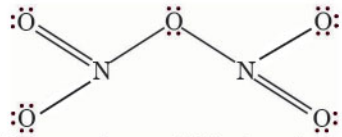
8. *Refer NCERT File Q. 19.*
9. *Refer NCERT File Q. 27. (c) and (b)*
10. *Refer NCERT File Q. 15.*
12. (*a*) *Refer Solved Example 7*
    (*b*) Lithium ion is very small ion and therefore, it has strong positive field around it. Therefore, it can stabilize only a small anion O^{2-}. Sodium is large and it can stabilize large anion O_2^{2-} whereas potassium and rubidium being very large in size can easily stabilize larger superoxide O_2^- ion.
    (*c*) *Refer NCERT File Q.29 (ii).*
13. (*a*) $Rb^+ > K^+ > Na^+ > Li^+$ because of lesser hydration of ion as size increases. In other words, hydrated radii of ions decrease as Li^+ , Na^+, K^+, Rb^+.
    (*b*) *Refer NCERT File Q.12.*

UNIT PRACTICE TEST–11

1. $SiCl_4$
2. Due to inert pair effect, lead shows an oxidation state of +2 and therefore, $PbCl_2$ is more stable than $PbCl_4$.
3. Six
4. $:\ddot{O}{=}C{=}\ddot{O}: \longleftrightarrow :\overset{+}{O}{\equiv}C{-}\overset{-}{\ddot{O}}: \longleftrightarrow :\overset{-}{\ddot{O}}{-}C{\equiv}\overset{+}{O}:$
5. Boric acid is not a protic acid because it does not ionise in water to give a proton. But it acts as a Lewis acid by accepting electrons from hydroxide ion.
   $B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$
6. *Refer NCERT File Q. 14.*
7. *Refer NCERT File Q. 3.*
8. *Refer NCERT File Q. 24.*
9. (*i*) *Refer Conceptual Questions* 2 *Q. 1.*
   (*ii*) *Refer Conceptual Questions* 2 *Q. 2.*
   (*iii*) *Refer Solved Example 25.*
10. *Refer NCERT File Q. 28.*
11. (*i*) $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 6HCl$
    (*ii*) $SiF_4 + 2HF \longrightarrow H_2SiF_6$
    (*iii*) $ZnO + CO \longrightarrow Zn + CO_2$
    (*iv*) $Al_2O_3.\ 2H_2O(l) + 2NaOH(aq) + H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq)$
    (*v*) $Pb + 2NaOH + 4H_2O \longrightarrow Na_2\ [Pb(OH)_6] + 2H_2$
    (*vi*) $2NaH + B_2H_6 \longrightarrow 2Na\ [BH_4]$

UNIT PRACTICE TEST–11A

1. N_2O_5 has the structure



   The covalence of N is four because it has four shared pair of electrons.
2. $4\overset{+3}{H_3}\overset{+3}{P}O_3 \longrightarrow 2\overset{+5}{H_3}\overset{+5}{P}O_4 + \overset{-3}{P}H_3$
3. $3CuO + 2NH_3 \xrightarrow{\text{heat}} 3Cu + N_2 + 3H_2O$
4. Phosphine is formed :
   $P_4 + 3NaOH + 3H_2O \xrightarrow{\text{Heat}} PH_3 + 3NaH_2PO_2$
5. Due to small size of Cl atom, five Cl atoms can be accommodated around P atom. But I is of large size and therefore, five I atoms cannot be accommodated around P atom. As a result, P–I bonds are weak and prefer to form PI_3 rather than PI_5.
7. Refer Text Fig. 16 and Fig. 17 page 11A/30.
8. (*i*) Both PCl_5 and PBr_5 have trigonal bipyramidal geometry. This is not regular structure and is not stable. Therefore, PCl_5 splits into more stable octahedral and tetrahedral structures.

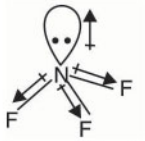
$$2PCl_5 \rightleftharpoons \underset{\text{Tetrahedral}}{[PCl_4]^+}\ \ \underset{\text{Octohedral}}{[PCl_6]^-}$$

But PBr_5 splits up into more stable tetrahedral structure.

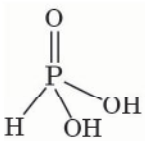
$$PB_5 \rightleftharpoons [PBr_4]^+\ [Br]^-$$

Since Br atoms are large, these six Br atoms cannot be accommodated around P atom to form octahedral structure.

(*ii*) In NF_3, the lone pair on N atom is on the opposite direction to N–F bond moments and therefore, it does not have donor properties like NH_3.



10. (*iii*) H_3PO_3 contains two P—OH bonds and therefore, its basicity is two.



12. (*i*) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
    (*ii*) $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$
    (*iii*) $2Ca_3(PO_4)_2 + 6SiO + 10C \longrightarrow P_4 + 6CaSiO_3 + 10CO$

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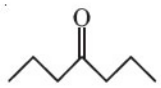
Solution File

UNIT PRACTICE TEST–12

1. 

   sp^3 sp^2 sp^2 sp
2. $CH_3—CH=CH—CN$
3. $(CH_3)_3C^+$
4. $Fe_4[Fe(CN)_6]_3$
5. $O_2NCH_2CH_2O^-$ is more stable because $–NO_2$ group has –I inductive effect and tends to disperse the –ve charge on the O atom. This results into stability. However, $CH_3CH_2^-$ group has +I inductive effect and tends to intensify the –ve charge and therefore, destabilizes it.
6. *Refer NCERT File Q. 11.*
7. $AgCl \equiv Cl$

   143.5 35.5

   143.5 g of AgCl contain Cl = 35.5

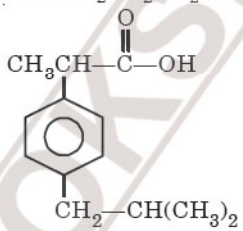
   0.628 g of AgCl contain Cl $= \frac{35.5}{143.5} \times 0.628$

   $= 0.155$ g

   % of chlorine $= \frac{0.155}{0.320} \times 100 = 48.43$ %
8. *Refer Solved Example 30.*
10. *Refer NCERT File Q. 20.*
11. (*i*) Pent-3-en-1-yne

    (*ii*) 4-(1,1-dimethylpropyl)-3-ethyl-4, 7-dimethyldecane

    (*iii*) 5, 6-Dimethylcyclohex-2-en-1-one
12. (*i*) $OHCCH_2CH_2CH_2CHO$

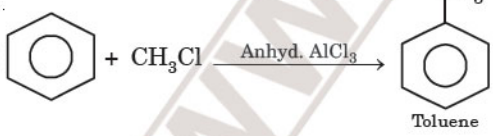
    (*ii*) 

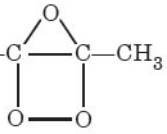
    (*iii*) $CH_3CH=CHCOOH$
13. (*a*) *Refer NCERT File Q. 29.*

    (*b*) *Refer Conceptual Questions 2 Q. 9.*

    (*c*) *Refer NCERT File Q.10.*

UNIT PRACTICE TEST–13

1. $CH_3CH_2COOH + 6HI \longrightarrow \underset{\text{Propene}}{CH_3CH_2CH_3} + 2H_2O + 3I_2$
2. 2-Methylpentane
3. $CH_2=CH—CH=CH_2$: Penta-2, 4-diene
4. Yes, it will show geometrical isomerism.
5. Cyclopentadienyl cation.
6. *Refer Solved Example 30.*
7. *Refer Solved Example 46 (ii).*
8. *Refer NCERT File Q. 25.*
9. *Refer NCERT File Q. 16.*
10. (*i*) 

    (*ii*) $CH_3C\equiv CCH_3 \xrightarrow{O_3}$  $\xrightarrow{Zn, H_2O}$ $\underset{\text{Butane-2, 3-dione}}{CH_3—\overset{\overset{O}{\|}}{C}—\overset{\overset{O}{\|}}{C}—CH_3}$

    (*iii*) $CH_3CH_2C\equiv CH \xrightarrow[\text{Heat}]{\text{acidic } KMnO_4} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + CO_2 + H_2O$
12. (*a*) *Refer Solved Example 28*

    (*b*) *Refer NCERT File Q.10.*

UNIT PRACTICE TEST–14

1. The amount of dissolved oxygen is less in warm water than in cold water.
2. Biological oxygen demand, chemical oxygen demand.
3. The chemical substances used to kill weeds or undesirable vegetation. *e.g.,* sodium arsenate.
4. Chlorofluorocarbon compounds.
5. Methyl isocyanate ($CH_3N=C=O$).
6. *Refer Conceptual Questions, Q.6.*
7. *Refer Conceptual Questions, Q.5.*
8. *Refer NCERT File Q. 19*
9. *Refer NCERT File Q. 5*
10. *Refer Conceptual Questions, Q. 10.*

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MOCK TEST – 2

1. benzoic acid
2. (*i*)
3. CCl_4 does not get hydrolysed while BCl_3 readily gets hydrolysed to boric acid.
   $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 6HCl$
4. Lithium
5. acetanilide
6. (*i*) LiH, CaH_2 : ionic hydrides
   (*ii*) NH_3, SiH_4 : covalent hydrides
7. Lithium is less electropositive than sodium and therefore, carbonate of lithium is less stable than that of sodium. Li_2CO_3 is not so stable to heat and therefore, decomposes at lower temperature. This is because lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of Li_2O and CO_2. On the other hand, Na_2CO_3 is very stable and decomposes at higher temperature.
8. *Refer Chapter 11 Conceptual Questions,* I *Q. 9*
9. (*i*) $CH_3—CH(CH_3)—CH_2$ (attached to benzene ring) and OH (attached to benzene ring)

   (*ii*) $OCH—CH_2—CH_2—CH_2—CH_2—CHO$
10. (*i*) 3, 3-Dimethylpentane
    (*ii*) 4-Hydroxy-3-methoxy benzaldehyde.
13. *Refer Chapter 12 Solved Example 36.*
18. (*i*) $CH_3—C\equiv C—Ph \xrightarrow[H_2O]{Hg^{2+},\ H^+} CH_3—CH=C(OH)—Ph \rightleftharpoons CH_3—CH_2—C(=O)—Ph$

    (*ii*) $(CH_3)_2C=CH_2 \xrightarrow{Br_2,\ H_2O} CH_3—C(CH_3)(OH)—CH_2Br$

    (*iii*) $CH_3CH_2C(CH_3)=CHCH_3 \xrightarrow[Zn,H_2O]{O_3,}$

    $CH_3CH_2—C(=O)—CH_3 + CH_3CHO$
19. *Refer Chapter 13 Solved Example 14.*
20. *Refer Chapter 11 Solved Example 20.*
22. (*b*) $CH_3CH=C(CH_2CH_3)_2$: 3-Ethylpent-2-ene
23. (*b*) *Refer NCERT File Chapter 13. Q. 1.*
24. (*b*) CO
27. (*c*) (*i*) $HC\equiv CH \xrightarrow{2NaNH_2} NaC\equiv CNa \xrightarrow{2CH_3Br}$

    Ethyne

    $CH_3C\equiv CCH_3$

    But-2-yne

    (*ii*) $CH_3CH=CH_2 \xrightarrow{HBr} CH_3CH(Br)CH_3 \xrightarrow[\text{Wurtz reaction}]{Na,\ ether}$

    Propene

    $CH_3CH(CH_3)—CH(CH_3)—CH_3$

    2,3-Dimethyl butane

    (*iii*) $CH_2=CH_2 \xrightarrow{Br_2,\ CCl_4} CH_2(Br)—CH_2(Br) \xrightarrow{2\text{ alc. KOH}}$

    Ethene

    $HC\equiv CH$

    Ethyne

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MOCK TEST – 3

1. In aqueous solution, sodium carbonate gets hydrolysed to give OH^- ions and hence it gives alkaline tests.

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$$

2. + 2.

3. $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b = 7$

4. $C_6H_5OH_2^+, NH_2NH_3^+$

5. endothermic

6. Peroxide ion has larger bond length.

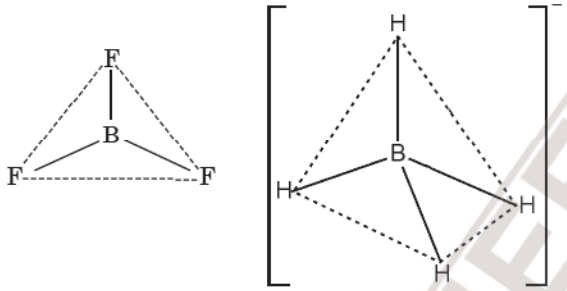
7. *Refer Conceptual Questions, Ch. 3. Q. 11.*

8. *Refer Chapter 2 Solved Example 53.*

9. *Refer Chapter 1 Solved Example 93.*

10. $$\log K = -\frac{\Delta G^\circ}{2.303\,RT}$$
$$= -\frac{-8.1}{2.308 \times 8.314 \times 10^{-3} \times 1000}$$
$$= 0.423$$
$$\therefore \quad K = \mathbf{2.64}$$

12. BF_3 is trigonal planar having sp^2 hybridisation. BH_4^- is tetrahedral having sp^3 hybridisation.



13. *Refer Conceptual Questions Chapter 12. Q. 14.*

15. (*i*) $CH_3CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl$ (Ethane)

$$\xrightarrow[\text{Wurtz reaction}]{2Na,\ ether} CH_3CH_2CH_2CH_3 \text{ (Butane)}$$

(*ii*) $CH_3CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl \xrightarrow{\text{alc. KOH}}$ (Ethane)

$$CH_2{=}CH_2 \xrightarrow{Br_2} CH_2(Br){-}CH_2(Br)$$
$$\downarrow \text{2 alc. KOH}$$
$$HC{\equiv}CH \text{ (Ethyne)}$$

(*iii*) $HC{\equiv}CH \xrightarrow[Hg^{2+}]{H^+,\ H_2O} CH_3CHO \xrightarrow{O} CH_3COOH$

$$\xrightarrow{NaOH} CH_3COONa$$
$$\downarrow NaO, CaO$$
$$CH_4$$

16. *Refer NCERT File Chapter 13, Q. (a) 17 and (b) Q. 10.*

18. (*i*) $Ca_3N_2\,(s) + 3H_2O(l) \longrightarrow 3Ca(OH)_2 + 2NH_3$

(*ii*) $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

(*iii*) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$

19. (*a*) *Refer Chapter 2 NCERT File Chapter 8, Q. 21.*

(*b*) *Refer NCERT File Chapter 8, Q. 27.*

20. (*a*) *Refer Chapter 2 Solved Example 39*

(*b*) 4

21. *Refer Chapter 1 Solved Example 119.*

22. (*b*) $-46.1\ kJ\ mol^{-1}$

24. (*a*) 10 volumes

(*b*) (*i*) $CaOCl_2 + H_2O_2 \longrightarrow CaCl_2 + H_2O + O_2$

(*ii*) $Fe_2(SO_4)_3 + H_2O_2 + 2NaOH \longrightarrow 2FeSO_4 + Na_2SO_4 + O_2 + 2H_2O$

25. (*c*) MgO

26. (*b*) *Refer Chapter 7 Solved Example 103.*

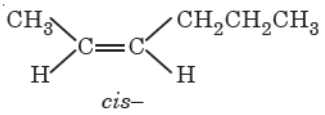
(*d*) *Refe Chapter 7 Solved Example 65.*

Or

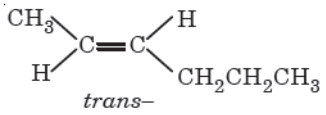
(*c*) 0.468

27. (*a*) *Refer Chapter 13 Solved Example 37.*

(*c*)



cis–



trans–

cis-hex-2-ene has higher dipole moment and therefore, will have stronger dipole–dipole interactions and hence higher boiling point.

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APPENDICES

C ORGANIC CONVERSIONS

D WHAT HAPPENS WHEN ?

E SOME ORGANIC COMPOUNDS POPULARLY KNOWN BY THEIR COMMON NAMES

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Appendix C

ORGANIC CONVERSIONS

A : Aliphatic Compounds

How will you convert?

1. Methane to ethane
2. Methane to ethanoic acid
3. Ethane to ethene
4. Ethane to ethyne
5. Ethane to ethylene glycol
6. Acetylene to acetic acid
7. Ethene to ethyne
8. Ethyne to propyne
9. Ethene to bromoethene
10. Propane to ethene
11. Ethyne to 2-butyne
12. Ethyne to propanone
13. Ethanoic acid to ethane
14. Ethyne to methane
15. Ethene to methanal
16. Ethene to ethanal
17. Propene to 2, 3-dimethylbutane
18. Propene to 1-propanol
19. Ethyne to benzene
20. Propyne to 1, 1-dibromopropane
21. Ethyne to dichloroethanal
22. Ethyne to 1,2 - dibromoethane
23. Acetic acid to methane
24. Acetylene to acetone
25. Ethyne to oxalic acid
26. Acetylene to 1 - butyne
27. Ethene to methanoic acid
28. Propene to 1– bromopropane

B : Aromatic Compounds

How will you convert?

1. Benzene to acetophenone
2. Toluene to benzene
3. Benzene to benzoic acid
4. Benzene to maleic anhydride
5. Benzoic acid to benzene
6. Benzene to *m*–nitrotoluene
7. Benzene to benzene hexachloride
8. Benzene to benzaldehyde
9. Benzene to *m*-nitrobenzoic acid
10. Acetylene to cyclohexane

A : Answers

1. *Methane to ethane*

$$\underset{\text{Methane}}{CH_4} \xrightarrow[\text{Sunlight}]{Cl_2} \underset{\text{Chloromethane}}{CH_3Cl} \xrightarrow[\text{Wurtz reaction}]{\text{Na, Ether}} \underset{\text{Ethane}}{CH_3CH_3}$$

Appendices

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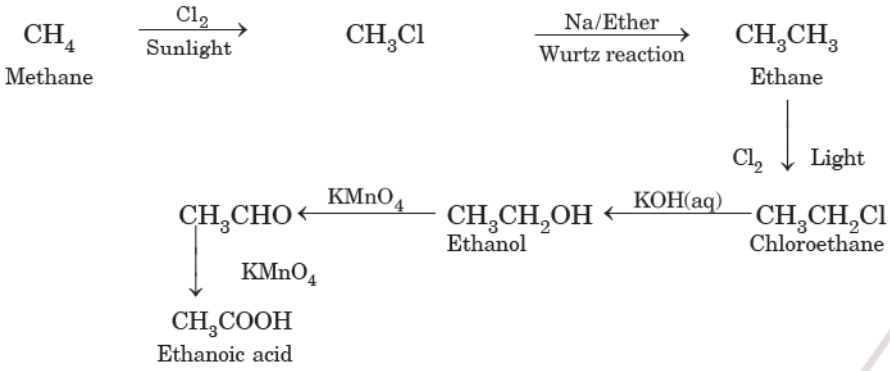
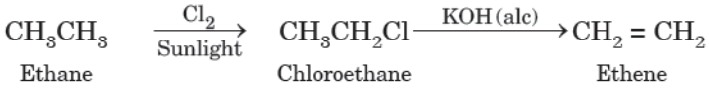
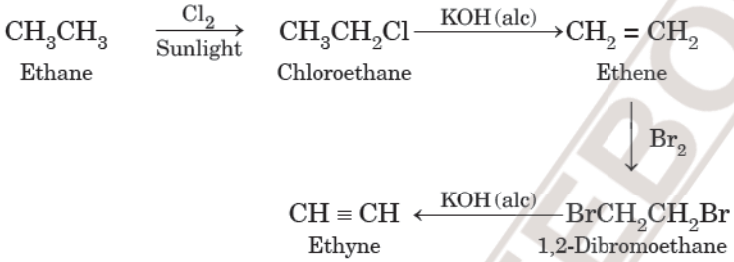
2. *Methane to ethanoic acid*



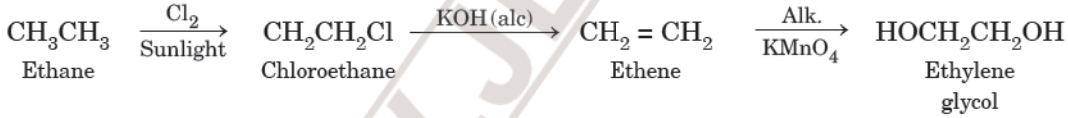
3. *Ethane to ethene*



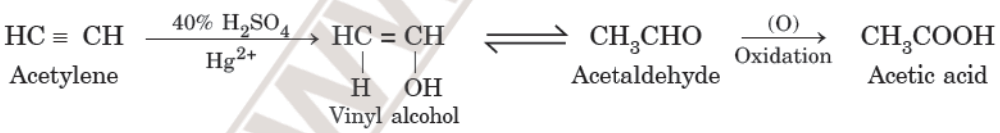
4. *Ethane to ethyne*



5. *Ethane to ethylene glycol*

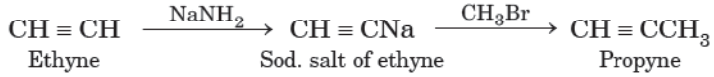


6. *Acetylene to acetic acid*

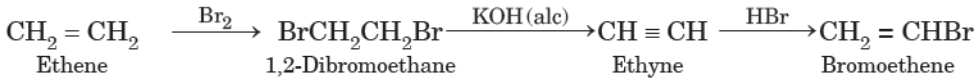


7. *Ethene to ethyne*

8. *Ethyne to propyne*



9. *Ethene to bromoethene*



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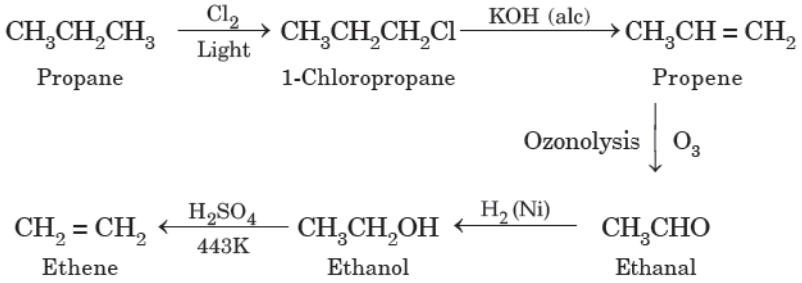
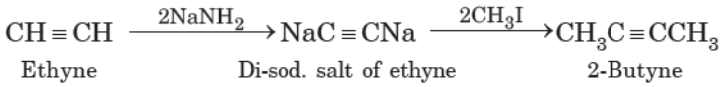
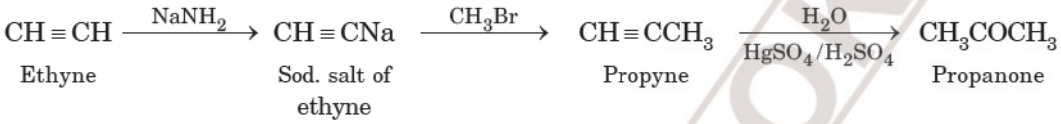
10. *Propane to ethene*



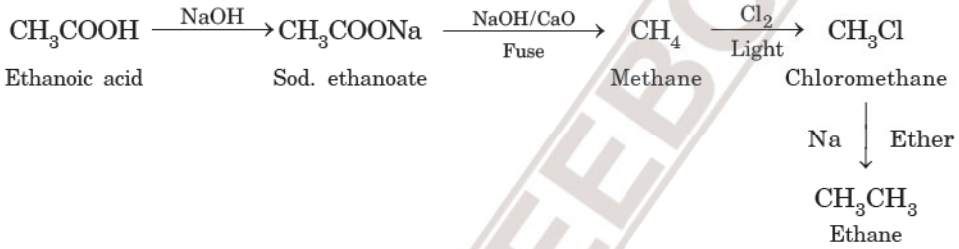
11. *Ethyne to 2-butyne*



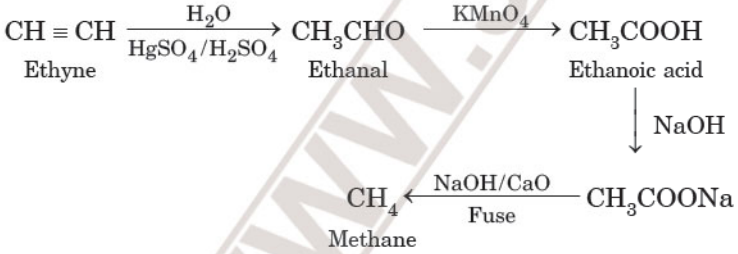
12. *Ethyne to propanone*



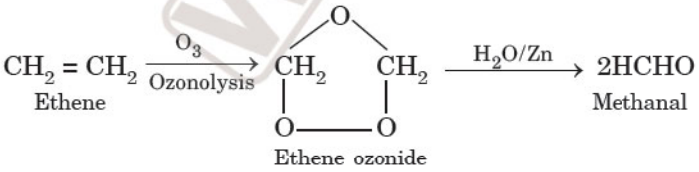
13. *Ethanoic acid to ethane*



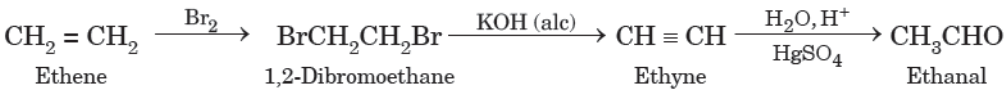
14. *Ethyne to methane*



15. *Ethene to methanal*



16. *Ethene to ethanal*



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17. *Propene to 2,3-dimethylbutane*

$$CH_3CH=CH_2 \xrightarrow{HBr} \underset{\text{2-Bromopropane}}{CH_3CH(Br)CH_3} \xrightarrow[\text{Wurtz reaction}]{\text{Na/Ether}} \underset{\text{2,3-Dimethylbutane}}{CH_3-CH(CH_3)-CH(CH_3)-CH_3}$$

Propene

18. *Propene to 1-propanol*

$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[(R-O-O-R)]{HBr} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow{KOH\ (aq)} \underset{\text{1-Propanol}}{CH_3CH_2CH_2OH}$$

19. *Ethyne to benzene*

$$\underset{\text{Ethyne}}{3\ CH\equiv CH} \xrightarrow[\text{(Polymerisation)}]{\text{Copper tubes}} \underset{\text{Benzene}}{C_6H_6}$$

20. *Propyne to 1, 1-dibromopropane*

$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow[(R-O-O-R)]{HBr} \underset{\text{1-Bromopropane}}{CH_3CH=CHBr} \xrightarrow[(R-O-O-R)]{HBr} \underset{\text{1,1-Dibromopropane}}{CH_3CH_2CHBr_2}$$

21. *Ethyne to dichloroethanal*

$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow{HClO} \underset{\text{Intermediate compound}}{[CH(OH)=CH(Cl)]} \xrightarrow{HClO} CH(OH)_2CHCl_2 \xrightarrow[\text{(Unstable)}]{H_2O} \underset{\text{Dichloroethanal}}{CHOCHCl_2}$$

22. *Ethyne to 1,2-dibromoethane*

$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[Pd/BaSO_4]{H_2} \underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{Br_2} \underset{\text{1,2-Dibromoethane}}{CH_2BrCH_2Br}$$

23. *Acetic acid to methane*

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} CH_3COONa \xrightarrow[CaO]{NaOH} \underset{\text{Methane}}{CH_4}$$

24. *Acetylene to acetone*

$$\underset{\text{Acetylene}}{HC\equiv CH} \xrightarrow{NaNH_2} HC\equiv CNa \xrightarrow{CH_3Cl} HC\equiv C-CH_3 \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

25. *Ethyne to oxalic acid*

$$\underset{\text{Ethyne}}{\overset{|||}{CH}\\CH} \xrightarrow[\text{Alkaline } KMnO_4]{4[O]} \underset{\text{Oxalic acid}}{\overset{\|}{COOH}\\COOH}$$

26. *Acetylene to 1 - Butyne*

$$\underset{\text{Ethyne}}{HC\equiv CH} \xrightarrow{NaNH_2} HC\equiv CNa \xrightarrow{CH_3CH_2Br} \underset{\text{1 – Butyne}}{HC\equiv C-CH_2\ CH_3}$$

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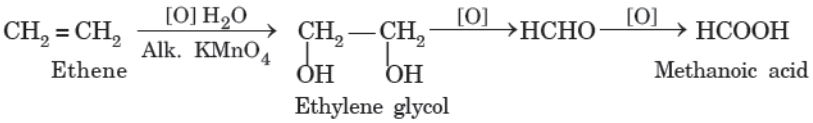
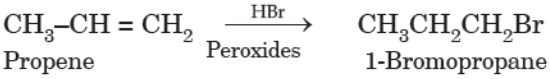
27. *Ethene to methanoic acid*

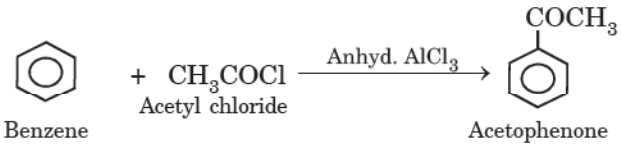


28. *Propene to 1– bromopropane*

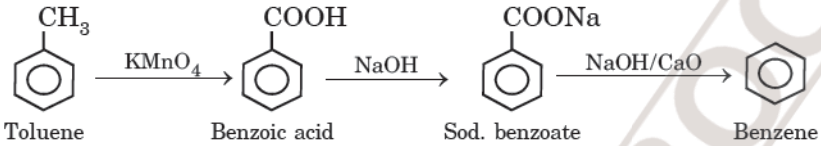


B : Answers

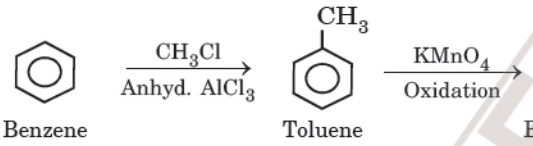
1. *Benzene to acetophenone*



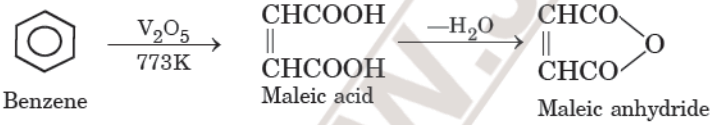
2. *Toluene to benzene*



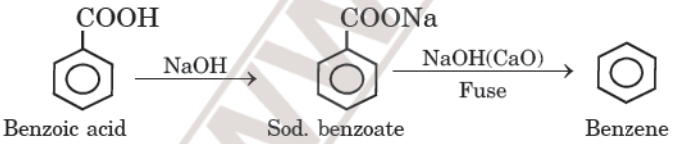
3. *Benzene to benzoic acid*



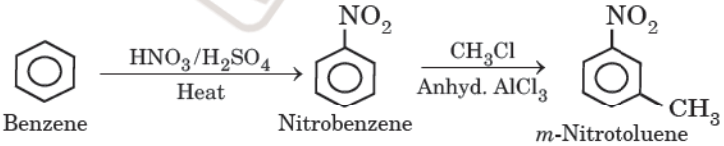
4. *Benzene to maleic anhydride*



5. *Benzoic acid to benzene*



6. *Benzene to m-nitrotoluene*



Appendices

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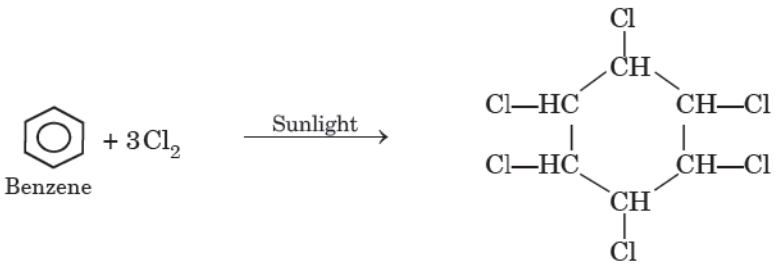
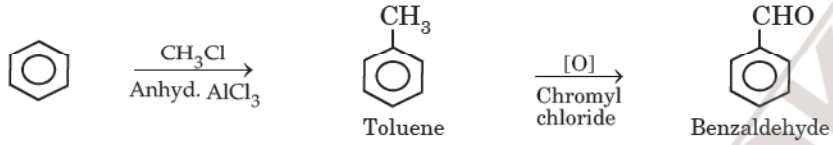
7. *Benzene to benzene hexachloride*

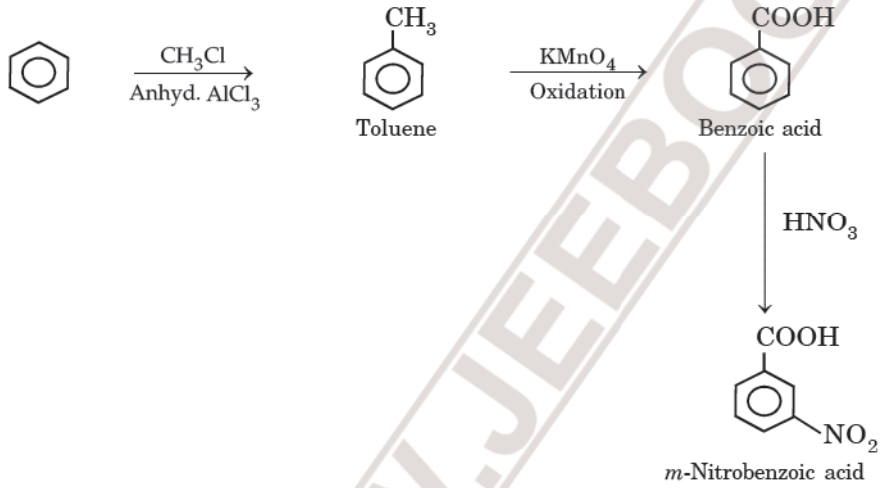


Benzene hexachloride (BHC)

8. *Benzene to benzaldehyde*

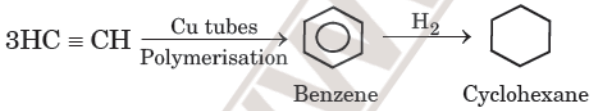


9. *Benzene to m-Nitrobenzoic acid*



m-Nitrobenzoic acid

10. *Acetylene to cyclohexane*



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Appendix D

WHAT HAPPENS WHEN ?

1. Ethylene is passed through alkaline potassium permanganate solution.
2. 2-Butene is treated with ozone followed by zinc dust and acid.
3. Propene reacts with water in the presence of mineral acid.
4. Ethyl chloride is treated with alcoholic caustic potash.
5. Benzene is treated with methyl chloride in the presence of anhydrous aluminium chloride.
6. Ethyne is bubbled into ammoniacal solution of cuprous chloride.
7. Propene is treated with HBr in the presence of peroxides.
8. Water is dropped over calcium carbide.
9. Water is added on ethyl magnesium bromide.
10. Benzene is heated with mixture of conc. HNO_3 and conc. H_2SO_4.
11. Toluene is treated with hot solution of potassium permanganate.
12. Sodium acetate is heated with soda lime.
13. Ethyl iodide is reduced.
14. Acetylene is heated to 773 K in copper tubes.
15. Ethylene dibromide is treated with zinc dust.
16. Benzene is treated with Cl_2 in the presence of $FeCl_3$.
17. Ethylene is treated with ozone.
18. Benzene is treated with chlorine in the presence of sunlight and absence of halogen carrier.
19. An aqueous solution of sodium salt of succinic acid is electrolysed.
20. Methane is mixed with oxygen and passed through heated molybdenum oxide.
21. Solution of ethylene in carbon tetrachloride is treated with chlorine at room temperature.
22. Propene is treated with hydrogen in the presence of Ni or Pt.
23. Propene is treated with Baeyer's reagent.
24. Styrene is polymerised.
25. Ethene is treated with excess of oxygen.
26. Propylene is treated with excess bromine in CCl_4.
27. Ethyne is oxidised with alkaline $KMnO_4$.
28. Propyne is treated with water in the presence of sulphuric acid and mercuric sulphate.
29. Acetylene is treated with ammoniacal silver nitrate solution.
30. Benzene is treated with sulphuric acid in the presence of sulphur trioxide.
31. Benzene is treated with acetyl chloride in the presence of anhydrous aluminium chloride.
32. Benzene is treated with hydrogen in the presence of Ni or Pt at 473-573 K.
33. Toluene is oxidised with chromyl chloride.
34. 2-methyl -2-butene is treated with ozone followed by reduction with hydrogen in the presence of zinc.
35. Mixture of methane and oxygen is compressed to 120 atm and passed through copper tubes at 475 K.
36. Ethane is treated with nitric acid in vapour phase.

Answers

1. Pink colour of $KMnO_4$ solution gets discharged and ethylene glycol is formed.

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + H_2O + O \xrightarrow{KMnO_4} \underset{\substack{OH \quad OH \\ \text{Ethylene glycol}}}{CH_2(OH)-CH_2(OH)}$$

2. Acetaldehyde is formed.

$$\underset{\text{2-Butene}}{CH_3-CH=CH-CH_3} \xrightarrow{O_3} CH_3-CH(-O-O-)CH-CH_3 \xrightarrow[H_2O]{Zn} 2CH_3CHO$$

(Acetaldehyde)

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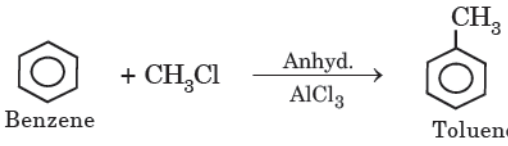
3. 2-Propanol is formed.

$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[H^+]{H_2O} \underset{\text{2-Propanol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3}$$

4. Ethene is formed.

$$\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + KOH\,(alc) \longrightarrow \underset{\text{Ethene}}{CH_2=CH_2} + KCl + H_2O$$

5. Toluene is formed.



6. A red precipitate of dicopper acetylide is formed.

$$\underset{\text{Ethyne}}{CH\equiv CH} + 2\,[Cu(NH_3)_2]Cl \longrightarrow \underset{\text{Red ppt.}}{CuC\equiv CCu} + 2NH_4Cl + 2NH_3$$

7. 1-Bromopropane is formed.

$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{Peroxides}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$$

The reaction proceeds according to anti-Markownikoff 's rule.

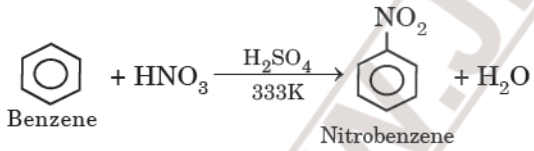
8. Acetylene is formed.

$$\underset{\text{Cal. carbide}}{CaC_2} + 2H_2O \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + Ca(OH)_2$$

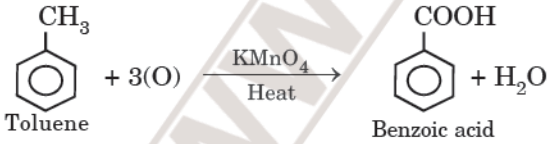
9. Ethane is formed.

$$\underset{\substack{\text{Ethyl magnesium}\\ \text{bromide}}}{C_2H_5MgBr} + H_2O \longrightarrow \underset{\text{Ethane}}{C_2H_6} + Mg(OH)Br$$

10. Nitrobenzene is formed.



11. Benzoic acid is formed.



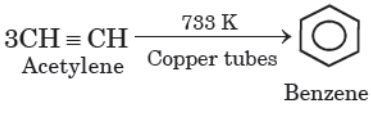
12. Methane is formed.

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \xrightarrow{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

13. Ethane is formed.

$$\underset{\text{Ethyl iodide}}{CH_3CH_2I} + 2H \xrightarrow{\text{Na, alcohol}} \underset{\text{Ethane}}{CH_3CH_3} + HI$$

14. Benzene is formed.



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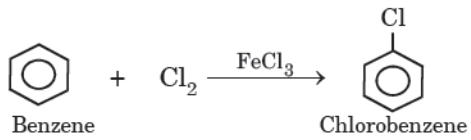
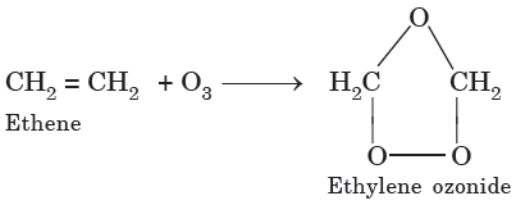
15. Ethene is formed.

$$\underset{\text{Ethylene dibromide}}{CH_2BrCH_2Br} \xrightarrow{Zn} \underset{\text{Ethene}}{CH_2 = CH_2} + ZnBr_2$$

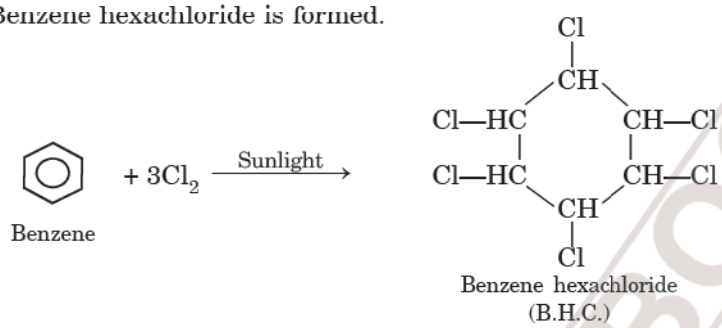
16. Chlorobenzene is formed.



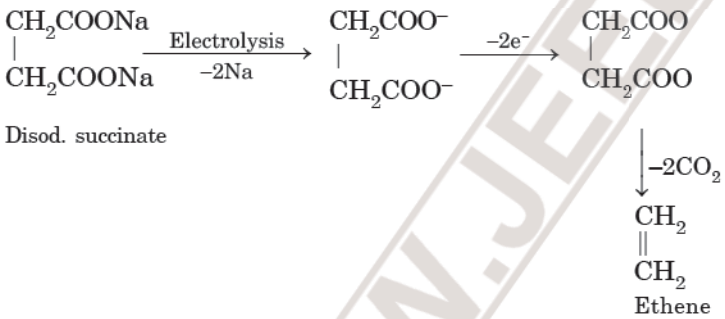
17. Ethylene ozonide is formed.



18. Benzene hexachloride is formed.



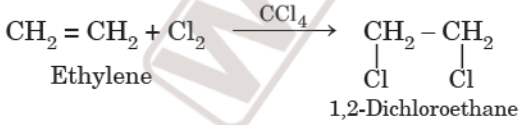
19. Ethene is obtained.



20. Formaldehyde is formed.

$$\underset{\text{Methane}}{CH_4} + O_2 \xrightarrow{MoO} \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

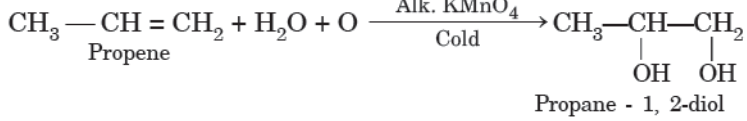
21. 1,2-Dichloroethane is formed.



22. Propane is formed.

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + H_2 \xrightarrow[473\ K]{Ni \text{ or } Pt} \underset{\text{Propane}}{CH_3—CH_2—CH_3}$$

23. Propane-1, 2 diol is formed.



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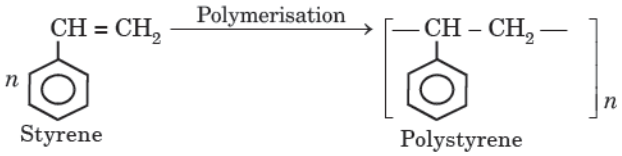
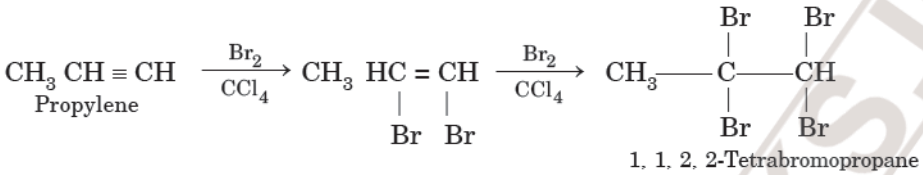
24. Polystyrene is formed.



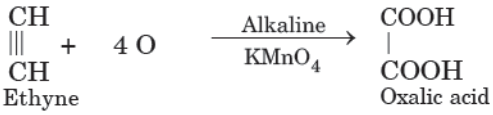
25. Carbon dioxide and water are formed.

$$\underset{\text{Ethene}}{C_2H_4} + 3O_2 \longrightarrow \underset{\text{Carbon dioxide}}{2CO_2} + \underset{\text{Water}}{2H_2O}$$

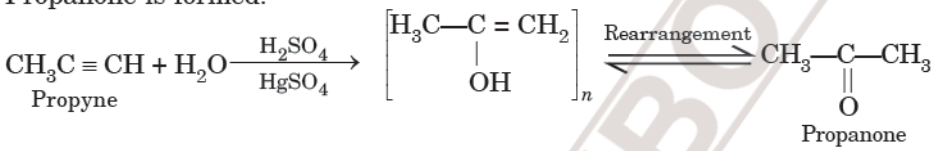
26. 1, 1, 2, 2 - Tetrabromopropane is formed.



27. Oxalic acid is formed.



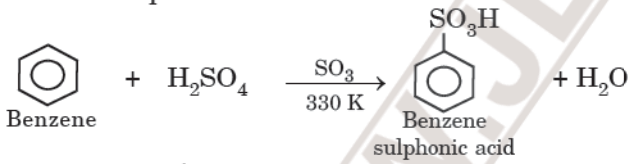
28. Propanone is formed.



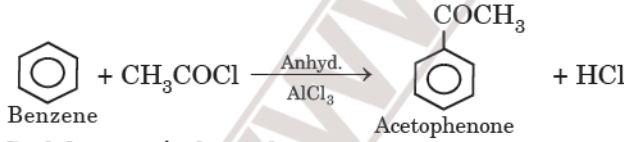
29. Disilver acetylide is formed.

$$\underset{\text{Acetylene}}{HC \equiv CH} + 2\,\underset{\substack{\text{Ammoniacal}\\ \text{silver nitrate}}}{[Ag(NH_3)_2]\,NO_3} \longrightarrow \underset{\text{Disilver acetylide}}{AgC \equiv CAg} + 2\,NH_4NO_3 + 2\,NH_3$$

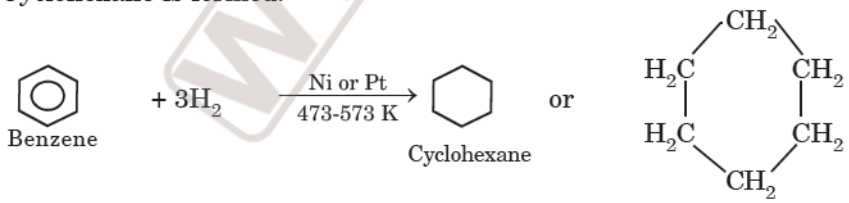
30. Benzene sulphonic acid is formed.



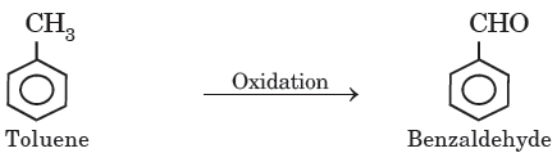
31. Acetophenone is formed.



32. Cyclohexane is formed.



33. Benzaldehyde is formed.



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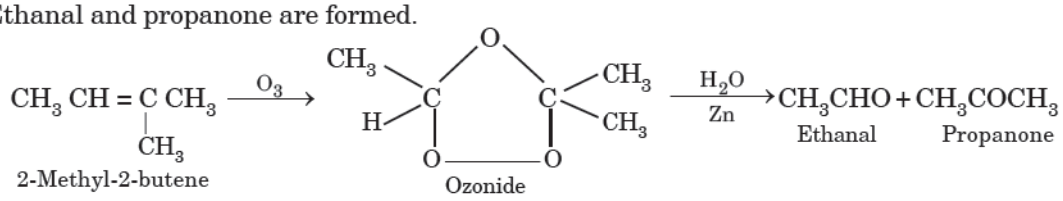
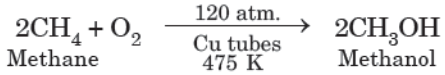
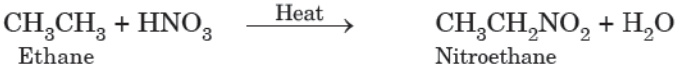
34. Ethanal and propanone are formed.



35. Methanol is formed.



36. Nitroethane is formed.



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Appendix E

SOME ORGANIC COMPOUNDS POPULARLY KNOWN BY THEIR COMMON NAMES

Acetylene	$HC \equiv CH$
Acetone	$CH_3-CO-CH_3$
Acetaldehyde	CH_3CHO
Formaldehyde	$HCHO$
Neo-pentane	$C(CH_3)_4$
Vinyl chloride	$CH_2 = CHCl$
Tert-amyl alcohol	$CH_3-C(CH_3)(OH)-CH_2-CH_3$
Iso-butyl bromide	$(CH_3)_2CHCH_2Br$
Acetonitrile	CH_3CN
Allyl alcohol	$CH_2 = CH - CH_2OH$
Glycerol	$CH_2(OH)-CH(OH)-CH_2(OH)$
Allyl bromide	$CH_2 = CH - CH_2Br$
Allene	$CH_2 = C = CH_2$
Propynyl iodide	$CH \equiv CCH_2I$
Crotyl bromide	$CH_3CH = CHCH_2Br$
Acrylic acid	$CH_2 = CHCOOH$
Acrolin	$CH_2 = CHCHO$
Ethylene glycol	$CH_2(OH)-CH_2(OH)$
Propylene glycol	$CH_3CH(OH)-CH_2(OH)$
Diazomethane	CH_2N_2
Glycolic aldehyde	$HOCH_2CHO$
Glyceraldehyde	$HOCH_2CHOHCHO$
Crotonaldehyde	$CH_3CH = CHCHO$
Formic acid	$HCOOH$
Acetyl acetone	$CH_3COCH_2COCH_3$
Valeric acid	C_4H_9COOH
Malonic acid	$CH_2(COOH)_2$
Oxalic acid	$(COOH)_2$
Crotonic acid	$CH_3CH = CHCOOH$
Succinic acid	$(CH_2COOH)_2$
Maleic acid	$HC(COOH) = HC(COOH)$ (*cis*)
Fumaric acid	$HC(COOH) = HC(COOH)$ (*trans*)
Malic acid	$CH(OH)(COOH)CH_2COOH$
Tartaric acid	$CH(OH)(COOH)CH(OH)COOH$
Citric acid	$HOOCCH_2C(OH)(COOH)CH_2COOH$
Glycine	NH_2CH_2COOH
Lactic acid	$CH_3CH(OH)COOH$
Glycolic acid	$CH_2(OH)COOH$
Glyoxalic acid	$CHO-COOH$
Acetamide	CH_3CONH_2

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LOGARITHMS

$\text{Log}_{10}N$

N	0	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529
18	2553	2577	2601	2625	2648	2672	2695	2618	2742	2765
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

ADD NUMBERS IN MEAN DIFFERENCE COLUMNS

MEAN DIFFERENCES								
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
5	9	13	17	21	26	30	34	38
4	8	12	16	20	24	28	32	36
4	8	12	16	20	23	27	31	35
4	7	11	15	18	22	26	29	33
3	7	11	14	18	21	25	28	32
3	7	10	14	17	20	24	27	31
3	6	10	13	16	19	23	26	29
3	7	10	13	16	19	22	25	29
3	6	9	12	15	19	22	25	28
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3	6	9	11	14	17	20	23	26
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3	6	8	11	14	16	19	22	24
3	5	8	10	13	16	18	21	23
3	5	8	10	13	15	18	20	23
3	5	8	10	12	15	17	20	22
2	5	7	9	12	14	17	19	21
2	4	7	9	11	14	16	18	21
2	4	7	9	11	13	16	18	20
2	4	6	8	11	13	15	17	19
2	4	6	8	11	13	15	17	19
2	4	6	8	10	12	14	16	18
2	4	6	8	10	12	14	15	17
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2	3	5	6	8	9	11	12	14
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1	3	4	5	7	8	9	11	12
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1	2	3	4	5	6	7	7	8
1	2	3	4	5	5	6	7	8
1	2	3	4	4	5	6	7	8
1	2	3	4	4	5	6	7	8
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
MEAN DIFFERENCES								

Example : *Log 473.7 = 2.6749 (for 473)*

+ 6 (mean diff. for 7)

2.6755

Mantissa

Characteristic

Log 0.004516 = $\bar{3}$.6542 (for 451)

+ 6 (mean diff. for 6)

$\bar{3}$.6548

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LOGARITHMS

Log_{10}N

N	0	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

ADD NUMBERS IN MEAN DIFFERENCE COLUMNS

MEAN DIFFERENCES								
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0	1	1	2	2	3	3	4	4
0	1	1	2	2	3	3	4	4
0	1	1	2	2	3	3	4	4
0	1	1	2	2	3	3	3	4
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
MEAN DIFFERENCES								

Some Rules

$\log (a) \times (b) = \log a + \log b$ $\qquad$ $\log (a)^n = n \log (a)$

$\log (a) / (b) = \log a - \log b$ $\qquad$ $\ln x = 2.303 \log x$

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ANTI-LOGARITHMS

10^x

x	0	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2524
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155
x	0	1	2	3	4	5	6	7	8	9

ADD NUMBERS IN MEAN DIFFERENCE COLUMNS

MEAN DIFFERENCES								
1	2	3	4	5	6	7	8	9
0	0	1	1	1	1	2	2	2
0	0	1	1	1	1	2	2	2
0	0	1	1	1	1	2	2	2
0	0	1	1	1	1	2	2	2
0	1	1	1	1	2	2	2	2
0	1	1	1	1	2	2	2	2
0	1	1	1	1	2	2	2	2
0	1	1	1	1	2	2	2	2
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	2	2	2	3	3
0	1	1	1	2	2	2	3	3
0	1	1	1	2	2	2	3	3
0	1	1	1	2	2	2	3	4
0	1	1	1	2	2	2	3	4
0	1	1	1	2	2	3	3	3
0	1	1	1	2	2	3	3	3
0	1	1	1	2	2	3	3	4
0	1	1	1	2	2	3	3	4
0	1	1	1	2	2	3	3	4
0	1	1	1	2	2	3	3	4
0	1	1	1	2	2	3	3	4
1	1	2	2	3	3	4	4	5
1	1	2	2	3	3	4	4	5
1	1	2	2	3	3	4	4	5
1	1	2	2	3	3	4	4	5
1	1	2	2	3	3	4	5	5
1	1	2	2	3	4	4	5	5
1	1	2	2	3	4	4	5	5
1	1	2	2	3	4	4	5	6
1	1	2	3	3	4	4	5	6
1	1	2	3	3	4	4	5	6
1	1	2	3	3	4	5	5	6
1	1	2	3	3	4	5	5	6
1	1	2	3	3	4	5	5	6
1	1	2	3	4	4	5	6	6
1	1	2	3	4	4	5	6	6
1	2	3	4	5	6	7	8	9
MEAN DIFFERENCES								

Example : *Antilog 1.3377 = 21.73 (for .337)*
+ 3 (mean diff. for 7)
21.76 (decimal after 2 s.f.)
Indicates that the decimal point must be placed after the first 2 figures.

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x	0	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063
.85	7079	7096	7112	7126	7145	7161	7178	7194	7211	7228
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977
x	0	1	2	3	4	5	6	7	8	9

ADD NUMBERS IN MEAN DIFFERENCE COLUMNS

MEAN DIFFERENCES								
1	2	3	4	5	6	7	8	9
1	1	2	3	4	4	5	6	7
1	2	2	3	4	5	5	6	7
1	2	2	3	4	5	5	6	7
1	2	2	3	4	5	6	6	7
1	2	2	3	4	5	6	6	7
1	2	2	3	4	5	6	7	7
1	2	3	3	4	5	6	7	8
1	2	3	3	4	5	6	7	8
1	2	3	4	4	5	6	7	8
1	2	3	4	5	5	6	7	8
1	2	3	4	5	6	6	7	8
1	2	3	4	5	6	7	8	9
1	2	3	4	5	6	7	8	9
1	2	3	4	5	6	7	9	10
1	2	3	4	5	7	8	9	10
1	2	3	4	6	7	8	9	10
1	2	3	5	6	7	8	9	10
1	2	4	5	6	7	8	9	11
1	2	4	5	6	7	8	10	11
1	2	4	5	6	7	9	10	11
1	3	4	5	6	8	9	10	11
1	3	4	5	6	8	9	10	12
1	3	4	5	7	8	9	10	12
1	3	4	5	7	8	9	11	12
1	3	4	5	7	8	10	11	12
1	3	4	6	7	8	10	11	13
1	3	4	6	7	9	10	11	13
1	3	4	6	7	9	10	12	13
2	3	5	6	8	9	11	12	14
2	3	5	6	8	9	11	12	14
2	3	5	6	8	9	11	13	14
2	3	5	6	8	10	11	13	15
2	3	5	7	8	10	12	13	15
2	3	5	7	8	10	12	13	15
2	3	5	7	9	10	12	14	16
2	4	5	7	9	11	12	14	16
2	4	5	7	9	11	13	14	16
2	4	6	7	9	11	13	15	17
2	4	6	8	9	11	13	15	17
2	4	6	8	10	12	14	15	17
2	4	6	8	10	12	14	16	18
2	4	6	8	10	12	14	16	18
2	4	6	8	10	12	15	17	19
2	4	6	8	11	13	15	17	19
2	4	7	9	11	13	15	17	20
2	4	7	9	11	13	16	18	20
2	5	7	9	11	14	16	18	20
1	2	3	4	5	6	7	8	9
MEAN DIFFERENCES								

Example : *Antilog 2.6459 =0.04416 (for .645)*
+ 9 (mean diff. for)
0.004425

A simple rule :

(*i*) If the characteristic is positive, then put the decimal after (n + 1) digits from the left
(*ii*) If the characteristic is negative, then put (n – 1) zeros before the first significant digit

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Useful Relations

$\pi = 3.1416$	$\ln X = 2.303 \log X$	$2.303\ RT/F = 0.05916\ V$
$e = 2.71828$	$2.303\ RT = 5709\ J\ mol$ (at 25°C)	(at 25°C)

Selected Greek letters

α	alpha	ξ	xi
β	beta	ν	nu
γ	gamma	Π, π	pi
Δ, δ	delta	ρ	rho
ε	epsilon	Σ, σ	sigma
η	eta	τ	tau
θ	theta	Φ, ϕ	phi
κ	kappa	χ	chi
Λ, λ	lambda	ψ	psi
μ	mu	Ω, ω	omega

Some Useful Conversion Factors

1 kg	=	1000 gram
1 gram	=	10 decigram
	=	100 centigram
	=	1000 milligram
1 litre	=	$1\ dm^3 = 10^3\ cm^3$
1eV	=	$1.6022 \times 10^{-19}\ J$
1 cal	=	$4.184\ J = 4.184 \times 10^7\ erg$
1 J	=	$10^7\ erg$
1 L. atm	=	$24.217\ cal = 101.32\ J$
1 Å	=	$10^{-8}\ cm = 10^{-10}\ m = 0.1\ nm$
1 atm	=	760 nm Hg
	=	1.013×10^5 pascals
1 bar	=	10^5 pascals

Prefixes

f	p	n	m	m	c	d	k	M
femto	pico	nano	micro	milli	centi	deci	kilo	mega

USEFUL PHYSICAL CONSTANTS

Quantity	Symbol	Value
Speed of light	c	$2.9979 \times 10^8\ m\ s^{-1}$
Atomic mass unit	amu or u	$1.6606 \times 10^{-27}\ kg$
Avogadro constant	N_A	$6.022 \times 10^{23}\ mol^{-1}$
Planck constant	h	$6.6262 \times 10^{-34}\ JK^{-1}$
Faraday constant	F	$9.64846 \times 10^4 C\ mol^{-1}$
Boltzmann constant	k	$1.3807 \times 10^{-23}\ JK^{-1}$
Charge-to-mass ratio of electron	e/m	$1.7588 \times 10^{11}\ C\ kg^{-1}$
Electronic charge	e	$1.60219 \times 10^{-19}\ C$
Gas constant	R	$8.314\ J\ mol^{-1}\ K^{-1}$
Molar volume (STP)	V_m	$22.414 \times 10^{-3}\ m^3\ mol^{-1}$
		$22.414\ dm^3\ mol^{-1}$
Mass of electron	m_e	$9.10953 \times 10^{-31}\ kg$
Mass of proton	m_p	$1.67265 \times 10^{-27}\ kg$
Mass of neutron	m_n	$1.67495 \times 10^{-27}\ kg$
Rydberg constant	R	$1.096 \times 10^7\ m^{-1}$

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- Large variety of SOLVED NUMERICAL PROBLEMS.
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- Additional information is given under 'Learning Plus','Key Note' and 'Watch Out'.
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